

1

3,759,846

DETERGENT COMPOSITION

Derek John MacDonald Robb, Bromborough, and John Raymond Samuel, Port Sunlight, England, assignors to Lever Brothers Company, New York, N.Y.
No Drawing. Filed Mar. 3, 1971, Ser. No. 120,745
Claims priority, application Great Britain, Mar. 16, 1970, 12,501/70

Int. Cl. C11d 3/066

U.S. Cl. 252—527

2 Claims 10

ABSTRACT OF THE DISCLOSURE

A fabric-washing detergent powder having superior fabric-softening properties, imparted by the presence in the composition of a water-insoluble soap in a very finely-divided form, is disclosed. A process for the manufacture of the composition, in which the water-insoluble soap is formed in situ in a slurry in the presence of a dispersing agent prior to spray-drying, is also disclosed.

The present invention relates to detergent compositions particularly suitable for washing fabrics and having fabric-softening properties.

Detergent compositions designed for fabric washing are generally based on a synthetic detergent active compound. Such compositions are superior in some respects to the soap-based compositions that they have replaced in most countries, but in one respect these compositions are inferior—the feel they impart to the washed fabric. This quality is important not only in respect of the sensation received when the article is touched or worn, but also in respect of the associated increased surface smoothness resulting in ease of ironing and improved draping qualities. The importance of fabric softening to the consumer is demonstrated by the steady growth of the market for fabric softeners designed to be applied in a rinse after a detergent composition has been employed to wash the fabrics concerned in a separate wash stage. A number of proposals have been made for compositions that would both clean and soften in a wash stage, but there is still a need for a composition that combines adequate detergency with effective softening. In particular, it has been proposed that conventional detergent compositions designed for fabric washing comprising a water soluble synthetic detergent active compound can be adapted to soften fabrics by the inclusion in the composition of a water-insoluble soap.

A detergent composition of the present invention comprises a synthetic detergent active compound and a water-insoluble soap in the form of aggregates of particles which aggregates have an average size of less than 2.5 microns, preferably less than 2 microns, as determined by the optical microscopy technique described herein.

If a detergent composition of the present invention is examined microscopically it is observed that the water-insoluble soap is present as aggregates of minute particles. The individual particles themselves are made up of large numbers of soap molecules, but these relatively compact particles group together in larger, less compact aggregates, and it is believed that it is these aggregates that are responsible for the fabric-softening properties imparted by the composition.

With the aid of various microscopy techniques that are described in detail below, it has been found that there is a close correlation between the average size of these soap particle aggregates and the overall fabric-softening ability of the composition in which they are present. It has been found that optimum fabric-softening is obtained when the water-insoluble soap particle aggregates have an aver-

2

age size of less than 2.5 microns, preferably less than 2 microns, as determined by the optical technique to be described below. Such an average soap particle aggregate size is well below that which is obtained by the use of normal methods of preparation, and requires the use of a special step to secure a reduction in the average aggregate size.

An embodiment of the present invention is a process for making a detergent powder containing a water-insoluble soap, in which process a hydrophilic dispersing agent is added to a slurry in which the water-insoluble soap is formed in situ, and the slurry is subsequently dried to produce the detergent powder.

In a particularly preferred embodiment of the invention, the hydrophilic dispersing agent is added to the slurry before the in situ formation of the water-insoluble soap. The hydrophilic dispersing agent is preferably a polyethylene glycol having a molecular weight of from about 200 to about 1000.

The synthetic detergent active compound can be any of the anionic, nonionic, zwitterionic or amphoteric materials conventionally used or recommended for fabric washing. Mixtures of synthetic detergent active agents may be used. The nature of these synthetic detergent active compounds is not an essential feature of the invention. The total synthetic detergent active content of a composition of the invention normally comprise from about 10 to about 35%, particularly from about 10 to about 20%, by weight of the composition. Suitable detergent active compounds include:

(a) Anionic detergent active agents: alkali-metal salts of organic sulphuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulphonic acid and sulphuric acid ester radicals (included in the term alkyl is the alkyl portion of higher acyl radicals) such as sodium or potassium alkyl sulphates, preferably those obtained by sulphating the higher alcohols (C_8 – C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene-sulphonates in which the alkyl group contains from about 9 to about 20 carbon atoms and in which the alkyl group is attached to the benzene ring in either the 1 position or at the secondary positions, such as in sodium linear alkyl (C_{10} – C_{15}) secondary benzene sulphonate, 2-phenyl-dodecane-sulphonate, 2-phenyl-octadecanesulphonate and 3-phenyl-dodecane-sulphonate; alkali-metal, preferably sodium, olefin sulphonate, i.e., the mixture of detergent active agents obtained when the products of the sulphonation of C_8 – C_{22} olefins (preferably substantially straight-chain alpha-olefins are neutralised and hydrolysed completely or almost completely; sodium alkyl glyceryl ether sulphonates, especially those ethers of the higher alcohols derived from tallow coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium or potassium salts of sulphur acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide per molecule and in which the alkyl radicals contain about 9 to about 18 carbon atoms; the reaction product of fatty acids esterified with isethionic acid and neutralised with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; and sodium or potassium salts of fatty acid amides of methyl taurine in which the fatty acids, for example, are derived from coconut oil.

(b) Nonionic synthetic detergent active agents: compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene

oxide with propylene glycol; the polyethylene oxide condensates of alkyl-phenols, e.g. the condensation products of alkylphenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkylphenols (the alkyl substituent in such compounds may be derived from polymerised propylene, isobutylene, octene, dodecene, or nonene, for example); those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine, such as compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said hydrophobic base having a molecular weight of the order of 2,500 to 3,000; the condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g. a coconut alcohol-ethylene oxide condensate having from 6 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms; long chain tertiary amine oxides corresponding to the following general formula $R_1R_2R_3N \rightarrow O$, wherein R_1 is an alkyl radical of from about 8 to 18 carbon atoms and R_2 and R_3 are each methyl, ethyl or hydroxyethyl radicals, such as dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyldodecylamine oxide, dimethyltetradecylamine oxide and dimethylhexadecylamine oxide, N-bis (hydroxyethyl) dodecylamine oxide; long chain tertiary phosphine oxides corresponding to the following formula $RR'R''P \rightarrow O$, wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms, such as dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetyl ethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, bis (hydroxymethyl) dodecylphosphine oxide, bis (2-hydroxyethyl) dodecylphosphine oxide, 2-hydroxypropylmethyltetradecylphosphine oxide, dimethylolelyphosphine oxide, and dimethyl-2-hydroxydodecylphosphine oxide; and dialkylsulphoxides corresponding to the following formula, $RR'S \rightarrow O$, wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxyalkyl radical containing one or two other oxygen atoms in the chain, the R groups ranging from 10 to 18 carbon atoms in chain length, and wherein R' is methyl, ethyl or alkylol; such as dodecyl methyl sulphoxide, tetradecyl methyl sulphoxide, 3-hydroxytridecyl methyl sulphoxide, 2-hydroxydodecyl methyl sulphoxide, 3-hydroxy-4-decyloxybutyl methyl sulphoxide, 3-hydroxy-4-dodecyloxybutyl methyl sulphoxide, 2-hydroxy-3-decyloxypropyl methyl sulphoxide, 2-hydroxy-3-dodecyloxypropyl methyl sulphoxide, dodecyl ethyl sulphoxide, 2-hydroxydodecyl ethyl sulphoxide, dodecyl-2-hydroxyethyl sulphoxide.

(c) Ampholytic synthetic detergent active agents which are derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, such as sodium-3 - dodecylaminopropionate, sodium-3-dodecylaminopropanesulphonate and sodium N-2-hydroxydodecyl-N-methyl-taurate.

(d) Zwitterionic synthetic detergent active agents, namely derivatives of aliphatic quaternary ammonium

compounds, sulphonium compounds and phosphonium compounds in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, such as 3 - (N,N - dimethyl - N - hexadecylammonio) propane-1-sulphonate, 3 - (N,N - dimethyl-N-hexadecylammonio) - 2 - hydroxypropane-1-sulphonate, 3-(dodecylmethylsulphonium) propane sulphonate, and 3-(cetyl-methylphosphonium) ethane sulphonate.

Further examples of non-soap detergent active agents commonly used in the art are given in "Surface Active Agents, vol. 1" by Schwartz and Perry (Interscience 1949) and "Surface Active Agents, vol. 2" by Schwartz, Perry and Berch (Interscience 1958).

The synthetic detergent active compound will generally, although not invariably, be associated with an equal or greater amount of a detergency builder such as sodium tripolyphosphate, sodium or potassium pyrophosphate, trisodium orthophosphate, sodium nitrilotriacetate, sodium ethylene diamine tetraacetate, polymeric detergency builders such as sodium salts of polycarboxylic acids and organic precipitant detergency builders such as sodium salts of straight chain alkyl or alkenyl succinic acids. In general, a detergent composition of the invention will contain from about 10 to about 60%, and particularly from about 25 to about 55%, by weight of detergency builder.

A detergent composition of the invention can also contain any of the other conventional ingredients of fabric-washing compositions, including lather boosters, such as alkylolamides of fatty acids derived from natural fats such as coconut oil and palm kernel oil, inorganic salts such as sodium sulphate and magnesium sulphate, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, chlorine-releasing bleaching agents such as trichloroisocyanuric acid and alkali-metal salts of dichloroisocyanuric acid, and, usually present in only minor amounts, perfumes, germicides, fluorescers, colourants, antiredeposition agents such as sodium carboxymethylcellulose, and enzymes.

The water insolubility of the soap will generally result from the soap having as its cation an alkaline earth metal such as calcium or magnesium, or less preferably, a metal such as aluminum that also forms insoluble soaps. The carboxylic acid forming the soap can be a straight-chain or branched-chain, saturated or unsaturated, monocarboxylic or polycarboxylic, natural or synthetic aliphatic acid, provided that the resultant soap is water-insoluble. Preferred carbon chain lengths are C_{16} - C_{22} . Examples of suitable carboxylic acids from which the soap may be derived are heptadecanoic (margaric), octadecanoic (stearic), nonadecanoic (n-nonadecylic), eicosanoic (arachidic), heneicosanoic and docosanoic (behenic) acids, and mixtures of these acids, and the mixtures of saturated and unsaturated fatty acids derived from natural fats and oils such as tallow, coconut oil, palm oil, palm kernel oil, babassu oil, groundnut oil and soft oil. These natural fatty acids may be hardened if desired, and a particularly preferred water-insoluble soap for use in a detergent composition of the invention is calcium hardened tallow soap.

The compositions of the invention can be prepared in any of the forms conventionally used or proposed for detergent compositions, such as sprayed-dried powders, granulates formed by agglomeration, flakes, tablets or bars.

A certain minimum amount of water-insoluble soap is required in the composition to achieve a perceptible fabric-softening effect. In part, this level of soap will depend on the concentration at which the detergent composition is used in contact with the fabric being washed, but, in general, from 2 to 25% by weight of the composition should comprise water-insoluble soap.

A detergent composition of the invention in powder form will normally be prepared by heat-drying a slurry in which the water-insoluble soap is present as small particles. The soap particles will be carried through into the dried composition although the drying process results in further aggregation of the slurry material. For example, in spray-drying, although a final composition typically contains granules of about 300–500 microns, these granules include as individual entities water-insoluble soap particle aggregates of an average size of less than 2.5 microns, and when the spray-dried granules disperse in water to form the wash solution these insoluble soap-particle aggregates are released.

It has been found the correlation between average size and fabric-softening ability applies not only to the soap particle aggregates but also to the individual soap particles themselves. These individual soap particles may be observed with the aid of an electron microscope, and it has been noticed that these individual soap particles are smallest in compositions with the greatest degree of fabric-softening ability.

A lower limit on soap particle and soap particle aggregate average size is set merely by the difficulties of obtaining particles or aggregates of such small sizes. Special methods of reducing the particle and particle aggregate average sizes have generally to be employed.

Methods that can be employed for reducing the average particle aggregate size of the water-insoluble soap are grinding in a colloid mill, or the use of ultrasonic techniques. However, for reasons of economy it is preferred to secure a reduced average particle aggregate size by controlling the formation of the water-insoluble soap in a slurry to be heat dried to form the final detergent composition. In this preferred method, the water-insoluble soap is formed by careful control of a reaction in the slurry of stoichiometric quantities of a water-soluble soap and a water-soluble salt which interact to produce a water-insoluble soap and another water-soluble salt by double decomposition.

In general it is preferred to have the water-soluble soap or the free fatty acid from which the soap is formed, dispersed with a major proportion of the ingredients of the final composition in an aqueous slurry and then to add the water-soluble salt to the slurry slowly. As a preferred variant of the process, the water-soluble soap is sodium hardened tallow soap and the water-soluble salt is calcium chloride.

A particularly preferred process for the preparation of a detergent composition of the invention involves the presence in the slurry during the formation of the water-insoluble soap of a hydrophilic dispersing agent such as polyethylene glycol. Experiments have shown that provided a certain level of polyethylene glycol is present in the slurry, no significant benefit results from raising this level. The slurry should contain at least 0.5%, and preferably at least 1% (based on the composition of the final detergent composition) of polyethylene glycol. Equal fabric-softening performance was achieved from detergent compositions prepared using polyethylene glycol 400 (i.e. polyethylene glycol of molecular weight 400) at the 6%, 2% and 1% level (based on the composition of the final detergent composition). Polyethylene glycols of other molecular weights have also been found to be suitable, such as polyethylene glycol 1000, polyethylene glycol 800 and polyethylene glycol 600. However, it is observed that the fabric-softening effect of the final detergent composition is greater if the lower molecular weight of polyethylene glycols are employed.

The following optical microscopy technique (known hereafter as the Samuel optical microscopy technique) was used to determine the average water-insoluble soap particle aggregate sizes. Accurate size measurement depends mainly on the quality of the image produced by the microscope. Three equally important factors deter-

mine the quality of the image: magnification, resolution and contrast.

An "Ortholux" German microscope was utilised in this technique. This microscope offers particularly favourable conditions for photomicrography since the photomicrograph can be taken without deflection of the image-forming beams. Also a micro electronic flash ("Mikroblitz 300") was used in conjunction with the above microscope.

Special phase contrast equipment was used in this technique as phase contrast microscopy can be helpful in the identification of particles and results in an improvement of definition and visibility, i.e. phase contrast objectives with normal absorption and a special condenser. Phase contrast utilises changes in the phase relationship between the light waves from the main image and from the secondary images of the light source for increasing the contrast of the image.

A transmitted beam of light was employed which passed through the sample from below via a mirror in the body of the microscope (to change the angle of the light) and a condenser which alters the contrast and magnification of the image when manipulated.

An aqueous solution (0.075%) of a sample of the particular detergent composition under investigation was placed on a "grid" for examination. A "grid" resembles a microscope slide in shape and size, the only difference being that the circular area in the centre of the slide is marked out with small squares or "graticules." These "graticules" have an individual area of $\frac{1}{400}$ mm.². When observing the sample through the binocular inclined eyepieces these graticules are plainly visible and these, together with the sample in focus, were photographed at two different magnifications ($\times 100$ and $\times 250$).

A Leitz 35 mm. camera with lens attachment (to fit the microscope) was used in conjunction with an electronic flash of 300 watts to "freeze" the soap particle aggregates, because in solution the very small particle aggregates exhibit Brownian motion. After photography of the magnified samples, slides were made and projected on to a screen. The length of a "graticule" or square on the grid was measured with a ruler and random particle aggregates were also measured. From this the size of the particle aggregates were determined.

The following examples illustrate the preparation of spray-dried detergent compositions of the invention and the assessment of their fabric-softening abilities.

EXAMPLES 1 AND 2

Three particulate detergent compositions having the following constitutions were prepared:

Ingredients	Percent by weight		
	A	Ex. 1	Ex. 2
Sodium dodecyl benzene sulphonate derived from a Shell alkylate DOBS 055.....	25	25	25
Sodium tripolyphosphate.....	35	35	35
Calcium soap/sodium chloride derived from stoichiometric quantities of sodium hardened tallow soap/calcium chloride.....	20	20	20
Anhydrous sodium silicate (Na ₂ O:SiO ₂ ratio 1:2).....	8	8	8
Sodium carboxymethylcellulose.....	0.5	0.5	0.5
Polyethylene glycol 400.....	0	2	2
Water to.....	100	100	100

Composition A was prepared by spray-drying a slurry containing the ingredients listed. The calcium chloride was added slowly to the hot slurry after the hardened tallow soap had been dissolved. The compositions of Examples 1 and 2 were prepared similarly, except that in the case of Example 1 the 2% of polyethylene glycol 400 was added to the slurry after the formation of the calcium soap, and in the case of Example 2 the 2% of polyethylene glycol 400 was added to the slurry before the formation of the calcium soap. Each composition was evaluated for its softening ability by the following proce-

5
10
15
20
25
30
35
40
45
50

pure. De-sized terry towelling was used. After washing in a particular formulation the towelling was dried in the open air and then placed in a humidity cabinet at 23° C. and 50% RH for 1 hour before being assessed by a panel. The panel was asked to rank the cloth in order of softness. A fresh unfelt surface was presented to each panel member for the test as the feel of a cloth changes with handling.

The evaluation of these compositions for softening ability showed the composition of Example 2 to be significantly better than the composition of Example 1 which in turn was significantly better than composition A.

When samples of the three compositions were subjected to the Samuel optical microscopy technique, previously described, the following average particle aggregate sizes were determined.

TABLE 1

Composition:	Average particle aggregate size (microns)
A	2.98±0.37
Example 1	2.48±0.48
Example 2	1.1±0.43

As can be seen from Table 1, the softening ability of the composition containing the smallest soap particle aggregates was greatest.

Samples of the three compositions were also examined by an electron microscopy technique. Grids for the microscope were prepared by ultra-centrifuging the water-insoluble soap particles onto a carbon-coated grid. The electron photomicrographs taken after conventional shadowing techniques showed that the individual entities picked out by the Samuel optical microscopy technique were in fact aggregates of much smaller particles. The sizes of the individual soap particles observed by the electron microscopy method were as follows:

Composition:	Particle size range (microns)
A	0.1-0.6
Example 1	0.05-0.1
Example 2	0.02-0.04

Thus it can be seen that the softening performance increased as the size of the individual soap particles decreased.

What is claimed is:

1. A process for the preparation of a particulate detergent composition consisting essentially of, by weight:

- (a) from about 10 to about 35% of a synthetic detergent active compound selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic detergent active compounds;

- (b) from about 2 to about 25% of a water-insoluble soap, the cation of said soap being selected from the group consisting of calcium and magnesium, said soap being derived from fatty acids selected from the group consisting of C₁₆ to C₂₂ linear unsaturated monocarboxylic acids, and mixtures thereof, and the mixtures of saturated and unsaturated fatty acids derived from natural fats and oils selected from the group consisting of tallows, coconut oil, palm oil, palm kernel oil, babassu oil, groundnut oil and soft oil, and said soap is in the form of aggregates of particles, said aggregates having an average size of less than 2.5 microns as determined by the Samuel optical microscopy technique; and

- (c) from about 10 to about 60% of a detergency builder selected from the group consisting of sodium tripolyphosphate, sodium pyrophosphate, trisodium orthophosphate, sodium nitrilotriacetate and sodium ethylenediaminetetraacetate,

in which process:

- (d) a hydrophilic dispersing agent, selected from the group consisting of polyethylene glycols having molecular weights of from about 200 to about 1000, is added to an aqueous slurry containing said synthetic detergent active and a water-soluble soap from which said water-insoluble soap is to be formed,

- (e) calcium chloride is added to said aqueous slurry so that a water-insoluble calcium soap is formed in situ, and

- (f) said aqueous slurry is then processed by spray-drying into said particulate detergent composition.

2. A process according to claim 1, wherein the amount of said hydrophilic dispersing agent employed in said slurry is at least 0.5% and not more than 6% by weight of the final detergent composition.

References Cited

UNITED STATES PATENTS

3,454,494	7/1969	Clark et al.	117-139.5 F
1,807,755	6/1931	Ryleg	117-139.5 F
1,963,974	6/1934	Ellis	117-139.5 F

OTHER REFERENCES

Marsh: An Intro. to Textile Finishing 1948, Chapman & Hall, pp. 259-265.

WILLIAM E. SCHULZ, Primary Examiner

U.S. Cl. X.R.

117-139.5; 252-8.6, 129