⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 091 802**
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: 83301989.6

㉒ Date of filing: 08.04.83

(51) Int. Cl.^{3}: C 11 D 3/00
C 11 D 3/37

㉚ Priority: 13.04.82 GB 8210701

㊸ Date of publication of application:
19.10.83 Bulletin 83/42

(84) Designated Contracting States:
BE DE FR GB IT NL

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BE DE FR IT NL

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(84) Designated Contracting States:
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(54) Foam-controlling detergent additive compositions and use thereof in detergent compositions.

(57) A detergent additive composition comprising a mixture of:

(a) a dispersion of polydimethylsiloxane foam-controlling agent in an ethoxylated nonionic surfactant having a hydrophilic-lipophilic balance of from 9 to 13 and a melting point of from 5°C to 36°C, and

(b) a dispersion of hydrophobic silica foam-controlling agent in a water-soluble or water dispersible organic carrier having a melting point of from 38°C to 90°C.

The additive composition is suitable for use in a detergent composition containing at least 12% of a mixture of anionic and nonionic surfactants to provide improved detergency and foam regulation characteristics across the range of wash temperature conditions.

Croydon Printing Company Ltd

FOAM-CONTROLLING DETERGENT ADDITIVE COMPOSITIONS AND USE THEREOF IN DETERGENT COMPOSITIONS

PHILLIP A. MORGAN

This invention relates to detergent compositions and their manufacture. In particular, it relates to heavy duty detergent compositions having controlled sudsing characteristics especially when used in automatic washing machines for washing clothes and the like.

Detergent compositions normally contain surfactants which tend to produce foam when agitated in aqueous solution. For many applications, especially in automatic washing and dishwashing machines, excess foam production is a serious problem and with many effective surfactants, it is necessary to add foam suppressing or controlling agents in order to prevent suds-overflow from the machine or under-usage of product by the user. On the other hand, consumers normally expect and prefer a certain amount of foam to be present and, indeed, research has shown that consumers are highly sensitive to a reduction in the foam level pattern. In any particular application, therefore, the optimum degree of foaming will be sufficiently low to avoid oversudsing under all conceivable washing machine temperature, load and soil conditions, but sufficiently high to meet the consumers preference for a moderate to generous level of foam.

Detergent compositions currently sold for the European domestic automatic washing machine market generally contain up to about 12% of organic surfactant and for such compositions, foam control agents satisfying the above constraints are now well established. For example, in European Patent application No 46342, it is taught to use a polydimethylsiloxane/hydophobic silica foam controller in the form of a dispersion in an ethoxylated nonionic surfactant using certain siloxane-oxyalkylene copolymers as dispersing agent. Once again, in European Patent Application No 8829, there is disclosed a foam-controlling system consisting of a major portion of wax together with a nonionic dispersing agent and hydrophobic silica.

In detergent compositions containing a high level of surfactant, however, (in excess of about 12%) problems of foam control in automatic washing machines become increasingly intractible. Thus, the technicque of dispersing polydimethylsiloxane/silica in nonionic surfactant is found to become impractical at high levels of foam-suppressor because of diminishing dispersion stability.

Moreover, the wax/silica/dispersant systems are also found to be deficient because of their inherently slow kinetics; in other words, the rate of release of wax/silica fails to match the rate of transport of surfactant to the air/water interface. Furthermore, these problems of foam control are found to be greatly exacerbated in concentrated surfactant systems containing a mixture of anionic and nonionic surfactant types which are known to have markedly differing foaming characteristics under varying wash temperature, product usage, soil, load and rinsing conditions.

The present invention thus provides a detergent composition containing a high level of organic surfactant and having improved foaming characteristics across the range of wash temperature conditions. It further provides a detergent composition containing a high level of a mixture of anionic and nonionic surfactants and having improved foaming under varying wash temperature, product usage, soil, load and rinsing conditions. It also provides a detergent additive composition suitable for addition to a high active heavy duty detergent composition to provide foam control characteristics.

According to the present invention, there is provided a detergent additive composition comprising

(a) a dispersion of polydimethylsiloxane foam-controlling agent in an ethoxylated nonionic surfactant, the nonionic surfactant having a hydrophilic- lipophilic balance (HLB) in the range from 9 to 13 and a melting point in the range from 5°C to 36°C, wherein the weight ratio of nonionic surfactant to polydimethylsiloxane is in the range from 10:1 to 100:1, and

(b) a dispersion of hydrophobic silica foam-controlling agent in a water-soluble or water-dispersible organic carrier having a melting point in the range from 38°C to 90°C, wherein the weight ratio of organic carrier to hydrophobic silica is in the range from 10:1 to 100:1,

and wherein the weight ratio of dispersion (a) to dispersion (b) is in the range from 1:1 to 50:1.

The additive composition thus comprises a mixture of preformed dispersions, a first dispersion (a) comprising polydimethylsiloxane (sometimes referred to herein as silicone) foam controlling agent in an ethoxylated nonionic surfactant of defined HLB (from 9 to 13, preferably from about 10 to about 12.5) and melting point (from 5°C to 36°C, preferably from about 10°C to about 28°C); and a second dispersion (b) comprising hydrophobic silica foam controlling agent in a water-soluble or water dispersible organic carrier also of defined melting point (from 38°C to 90°C). In highly preferred compositions, the organic carrier comprises a second ethoxylated nonionic surfactant having an HLB in the range from about 13.5 to about 19, preferably from about 15 to about 17.5, and a melting point in the range from about 38°C to about 60°C, preferably from about 40°C to about 55°C.

Although a silicone is an essential component of dispersion (a) and hydrophobic silica is an essential component of dispersion (b), it is also envisaged that dispersion (a) can additionally contain a proportion of hydrophobic silica and dispersion (b) can additionally contain a proportion of silicone. With regard to the silicone and hydrophobic silica content of dispersion (a), it is preferred that the weight ratio of silicone to silica is greater than about 20:1, and is preferably from about 25:1 to about 100:1; also that the weight ratio of hydrophobic silica in dispersion (b) to that in dispersion (a) is greater than about 1:2, and is preferably from about 10:1 to about 1:1. With regard to the silicone content of dispersion (b), on the other hand, it is preferred that the weight ratio of silicone in dispersion (b) to that in dispersion (a) is less than about 10:1 and is preferably from about 0.1:1 to about 5:1.

The weight ratio of nonionic surfactant to silicone in dispersion (a) and of organic carrier to hydrophobic silica in dispersion (b) is also of importance for reasons of stability and dispersibility. Thus, in dispersion (a), the weight ratio of nonionic surfactant to silicone is from 10:1 to 100:1, preferably from about 15:1 to about 40:1; in dispersion (b), the weight ratio of organic carrier to hydrophobic silica is in the range from 10:1 to 100:1, preferably from about 15:1 to about 50:1.

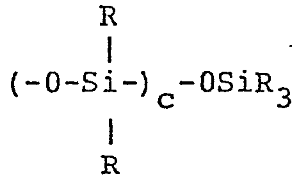
Desirably, the stability of polydimethylsiloxane in dispersion (a) is maintained with the aid of a dispersion agent, preferably a siloxane-oxyalkylene copolymer having the general formula I:

$$R_aSiY_{4-a} \qquad \text{I}$$

wherein a is 0 or an integer from 1 to 3, R is an alkyl group containing from 1 to 30 carbon atoms, or a group of formula II:

$$R'(OR')_bOR'' \qquad \text{II}$$

wherein R' is an alkylene group containing from 1 to 6 carbon atoms, b has a value of from 1 to 100; and R" is a capping group which is selected from hydrogen, alkyl, acyl, aryl, alkaryl, aralkyl or alkenyl groups containing up to 20 carbon atoms, sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate or isocyanate groups, or mixtures thereof; Y is a group having the formula III:-



$$(-O-\underset{R}{\overset{R}{Si}}-)_c-OSiR_3 \qquad \text{III}$$

wherein R is as defined above and c has a value from 1 to 200; and wherein at least one R group in the compound has the formula II. The weight ratio of polydimethylsiloxane in dispersion (a) to the siloxane-oxyalkylene copolymer is preferably in the range from about 2:1 to about 20:1, more preferably from about 5:1 to about 15:1.

As mentioned previously, the organic carrier component of dispersion (b) preferably comprises an ethoxylated nonionic surfactant having an HLB of from about 13.5 to about 19. Other suitable organic carrier components, however, include polyethyleneglycols having a molecular weight of from about 1500 to about 40,000 and, microcrystalline waxes. The latter are foam-controlling agents in their own right and are preferably added at a weight ratio of wax to silica of from about 20:1 to about 1:1, more preferably from about 15:1 to about 2:1. In the case both of the microcrystalline waxes and the polyethyleneglycols, the organic carrier preferably comprises at least about 35%, more preferably at least about 45% of ethoxylated nonionic surfactant in order to promote transport of silica to the air/water interface and, in the case of wax, to provide the necessary degree of water dispersibility.

The detergent additive compositions of the invention are utilized herein for making foam-controlled detergent compositions, either by premixing dispersion (a) and dispersion (b) prior to adding the remainder of the detergent composition, or by separately admixing dispersion (a) and dispersion (b) with the remainder of the detergent composition. The detergent additive composition generally constitutes from about 1% to about 30%, preferably from about 4% to about 25% of the total composition with dispersion (a) generally constituting from about 0.9% to about 25%, preferably from about 3.7% to about 23%, and dispersion (b) generally constituting from about 0.1% to about 5%, preferably from about 0.3% to about 2% by weight of tht total composition. The additive compositions are particularly valuable for use in detergent compositions containing anionic surfactant which is generally present in such compositions at level of from about 3% to about 30%, preferably from about 5% to about 20%, more preferably from about 8% to about 15%, with a total level of anionic and ethoxylated nonionic surfactants in the range from about 12% to about 50%, preferably from about 14% to about 30%.

With regard to the foam-controlling agents, the polydimethylsiloxane component preferably comprises, in total, from about 0.05% to about 0.75%, more preferably from about 0.3% to about 0.5% by weight of detergent composition and from about 1% to about 30%, more preferably from about 3% to about 12% by weight of additive composition; while the hydrophobic silica component preferably comprises, in total, from about 0.003% to about 0.045%, more preferably from about 0.008% to about 0.025%, by weight of detergent composition and from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of additive composition. The weight ratio of total polydimethylsiloxane: total hydrophobic silica, on the other hand, preferably lies in the range from about 3:1 to about 100:1, more preferably from about 10:1 to about 60:1.

In terms of processing, the detergent compositions of the invention are preferably made by forming dispersion (a) as a fluid high shear mixture of polydimethylsiloxane in the first nonionic surfactant, forming dispersion (b) as a particulate mixture of hydrophobic silica in the organic carrier, spraying dispersion (a) in fluent form onto a detergent base powder composition, and finally dry mixing dispersion (b) in powder form. A suitable base powder composition comprises anionic surfactant and detergency builder in amounts such that the final detergent composition contains from about 30% to about 99% base powder, from about 3% to about 30% anionic surfactant and from about 5% to abut 96% detergency builder.

Dispersion (b) can be rendered in powder form by agglomerating a molten mix of the dispersion with an inorganic salt in, for example, a pan agglomerator, fluidized bed, Schugi mixer or the like. A preferred inorganic salt is sodium tripolyphosphate. The particle size of the resulting agglomerate is preferably from about 0.5mm to 2mm, especially from about 0.84 to 1.4mm. Alternately, dispersion (b) can be rendered in powder form by extrusion.

The nonionic surfactant component of dispersion (a) and the organic carrier of dispersion (b) have melting points in the ranges from 5°C to 36°C, preferably from about 7°C to about 32°C, and from 38°C to 90°C, preferably from 40°C to 55°C respectively. In this context, the melting point is taken to refer to the temperature at which melting is completed. Conveniently, this temperature can be determined by thermal analysis using a Dupont 910 Differential Scanning Calorimeter with Mechanical Cooling Accessory and R90 Thermal Analyser as follows. A 5-10 mg sample of the material containing no free water or solvent, is encapsulated in a hermetically sealed pan with an empty pan as reference. The sample is initially heated until molten and then rapidly cooled (at about 20-30°C/min) to -70°C. Thermal analysis is then carried out at a heating rate of 10°C/min using sufficient amplification of ΔT signal (ie temperature difference between sample and reference - vertical axis) to obtain an endotherm-peak signal:baseline noise ratio of better than 10:1. The melting completion temperature is then the temperature corresponding to the intersection of the tangential line at the steepest part of the endotherm curve at the high temperature end of the endotherm, with the horizontal line, parallel to the sample temperature axis, through the highest temperature endotherm peak.

The organic carrier component of dispersion (b) can also be defined by the temperature at which onset of melting occurs. Preferably, the melting onset temperature is at least about 36°C, more preferably at least about 38°C. The melting onset temperature can once again be determined by thermal analysis as described above and is taken to be the sample temperature at the point of intersection of the base line with a tangent to the steepest part of the endotherm nearest the low temperature end of the endotherm.

The individual components of the invention will now be discussed in detail.

The nonionic surfactants suitable for use in dispersion (a) are condensates of ethylene oxide with a hydrophobic moiety providing a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 9 to 13, preferably from about 10 to about 12.5. The hydrophobic moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 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 3 to 14, preferably 5 to 12 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 9 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and di-isooctylphenol condensed with 12 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from about 2 to about 12 moles, preferably 2 to about 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Lutensols, Dobanols and Neodols which have about 25% 2-methyl branching (Lutensol being a Trade Name of BASF, Dobanol and Neodol being Trade Names of Shell), or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7,

Dobanol 45-9, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 12, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 15 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the Trade Name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

Especially preferred nonionic surfactants for use in dispersion (a) are the C_9-C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{12}-C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol.

The organic carrier component of dispersion (b) is preferably also based on an ethoxylated nonionic surfactant, but one having an average HLB in the range from about 13.5 to about 19, preferably from about 15 to about 17.5 and having a melting point in the range from about 38°C to about 60°C, preferably from about 40°C to about 55°C. Suitable nonionic surfactants are the condensation products of the primary or secondary alcohols having from about 15 to about 24 carbon atoms, in either straight chain or branched chain configuration, with from about 14 to about 100, preferably from about 20 to about 40 moles of ethylene oxide per mole of aliphatic alcohol. Examples of surfactants of this type are the condensation products of hardened tallow alcohol with an average of between about 20 and about 40 moles, preferably about 25 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms.

The polydimethylsiloxane foam controlling agent used herein are high molecular weight polymers having a molecular weight in the range from about 200 to about 200,000, and having a kinematic viscosity in the range from about 20 to 2,000,000 mm^2/s, preferably from about 500 to to about 50,000 mm^2/s, more preferably from about 3,000 to about 30,000 mm^2/s at 25°C. The siloxane polymer is generally end-blocked either with trimethylsilyl or hydroxyl groups but other end-blocking groups are also suitable. The polymer can be prepared by various techniques such as the hydrolysis and subsequent condensation of dimethyldihalosilanes, or by the cracking and subsequent condensation of dimethylcyclosiloxanes.

The hydrophobic silica foam controlling agent employed in the present composition preferably has a particle size of not more than about 100 millimicrons and a specific surface area in excess of about 50 m^2/g. Highly preferred materials have a particle size from about 10 millimicrons to about 20 millimicrons. The hydrophobic silica can be made, for example, by reacting fumed silica with a trialkyl chlorosilane (i.e., "silanated") to affix hydrophobic trialkylsilane groups on the surface of the silica. In a preferred and well known process, fumed silica is contacted with trimethylchlorosilanes.

Combinations of silicone and silica can also be used, both in dispersion (a) and in dispersion (b). Such combinations of silicone and silica can be prepared by affixing the silicone to the surface of silica for example by means of the catalytic reaction disclosed in US Patent 3,235,509. Suds controlling agents comprising mixtures of silicone and silica prepared in this manner preferably comprise, in dispersion (a), silicone and silica in a silicone:silica ratio of from about 20:1 to about 200:1, more preferably about 25:1 to about 100:1. The silica can be chemically and/or physically bound to the silicone in an amount which is preferably about 0.5% to 5% by weight, based on the silicone. In dispersion (b), mixed silicone/silica foam controlling agents can have a silicone:silica ratio of from about 1:1 to about 60:1, preferably from about 10:1 to about 50:1.

A preferred foam-controlling mixture herein comprises a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from about 10 millimicrons to 20 millimicrons and a specific surface area above about 50 m^2/g intimately mixed with a dimethyl silicone fluid having a molecular weight in the range of from about 500 to about 200,000.

Yet another foam-controlling mixture suitable herein comprises polydimethylsiloxane fluid, a silicone resin and silica. The silicone "resins" used in such compositions can be any alkylated silicone resins, but are usually those prepared from methylsilanes. Silicone resins are commonly described as "three-dimensional" polymers prepared from the hydrolysis of dichlorosilanes. The silica components of such compositions are the microporous materials such as the fumed silica aerogels and xerogels having the particle sizes and surface areas herein-above disclosed.

Mixed polydimethylsiloxane fluid/silicone resin/ silica materials suitable for use in the present compositions can be prepared in the manner disclosed in US Patent 3,455,839. These mixed materials are commercially available from the Dow Corning Corporation. Suitable materials of this type comprise:

(a) from about 10 parts to about 100 parts by weight of a polydimethylsiloxane fluid having a viscosity in the range from 20 to 30,000 mm/s at 25°C;

(b) 5 to 50 parts by weight of a siloxane resin composed of $(CH_3)_3SiO_{1/2}$ units and SiO_2 units in which the ratio of the $(CH_3)_3SiO_{1/2}$ units to the SiO_2 units is within the range of from 0.6:1 to 1.2:1; and

(c) 0.5 to 5 parts by weight of a silica aerogel.

Such mixtures can also be sorbed onto and into a water-soluble solid.

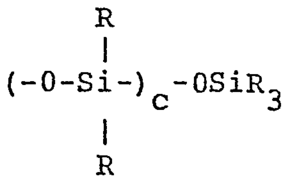
The siloxane-oxyalkylene copolymer dispersing agent suitable for use herein has the general formula I:

$$R_aSiY_{4-a} \qquad \text{I}$$

wherein a is 0 or an integer from 1 to about 3, R is an alkyl group containing from 1 to about 30 carbon atoms, or a group of formula II:

$$R'(OR')_bOR'' \qquad \text{II}$$

wherein R' is an alkylene group containing from 1 to about 6 carbon atoms, b has a value of from 1 to about 100, preferably from 10 to 30; and R" is a capping group which can be selected from hydrogen, alkyl, acyl, aryl, alkaryl, aralkyl or alkenyl groups containing up to about 20 carbon atoms, sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate or isocyanate groups, or mixtures thereof; Y is a group having the formula III:-



$$(-O-\underset{\displaystyle R}{\overset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}}-)_c-OSiR_3 \qquad \text{III}$$

wherein R is as defined above and c has a value from 1 to about 200; and wherein at least one R group in the compound has the formula II.

Preferred dispersing agents of the above type are selected from copolymers having the general formulae IV to VII:

$$R'''_a\mathrm{Si}[(\mathrm{OSiMe}_2)_p(\mathrm{OSiMeG})_q\mathrm{OSiMe}_2\mathrm{G}]_{4-a} \qquad \mathrm{IV}$$

$$R'''_a\mathrm{Si}[(\mathrm{OSiMe}_2)_p(\mathrm{OSiMeG})_r\mathrm{OSiMe}_3]_{4-a} \qquad \mathrm{V}$$

$$\mathrm{GMe}_2\mathrm{Si}(\mathrm{OSiMe}_2)_p(\mathrm{OSiMeG})_q\mathrm{OSiMe}_2\mathrm{G}, \text{ and} \qquad \mathrm{VI}$$

$$\mathrm{Me}_3\mathrm{Si}(\mathrm{OSiMe}_2)_p(\mathrm{OSiMeG})_r\mathrm{OSiMe}_3 \qquad \mathrm{VII}$$

wherein R''' is a C_{1-10} alkyl group, Me is methyl, G is the group of formula II, a has a value of 0 or 1, p has a value of at least 1, q has a value of 0 to about 50 and r has a value of 1 to about 50. Preferred dispersants contain G groups in non-terminal positions and contain a mixture of oxyethylene and oxypropylene groups, particularly in about a 1:1 ratio. Highly preferred are dispersants of formula VII having p+r from about 30 to about 120 with the ratio p:r from about 2:1 to about 8:1.

Suitable microcrystalline waxes for inclusion in dispersion (b) have a melting point in the range from about 35°C-115°C, preferably from about 65°C to about 100°C, a saponification value of less than 100, a molecular weight in the range 400-1000, and a penetration value of at least 6, measured at 77°C by ASTM-D1321. Suitable examples include microcrystalline and oxidised microcrystalline waxes; Fischer-Tropsch and oxidised Fischer-Tropsch waxes; ozokerite, ceresin, montan wax, beeswax, candellila and carnauba wax.

The compositions of the invention can be supplemented by all manner of detergent components. A highly preferred additional component is from about 3% to about 30% of anionic surfactant.

The anionic surfactant may be any one or more of the materials used conventionally in laundry detergents. Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulphonates, alkyl sulphates, alkyl polyethoxy ether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulpho-carboxylates and their esters, alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, alkyl phenol polyethoxy ether sulphates, 2-acyloxy alkane-1-sulphonate, and beta-alkyloxy alkane sulphonate.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents which form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C_{8-18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from about 9 to about 15, especially about 11 to about 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S.P. 2,220,099 and 2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS.

Other anionic detergent compounds herein include the sodium C_{10-18} alkyl glyceryl ether sulphonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulphonates and sulphates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulphate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

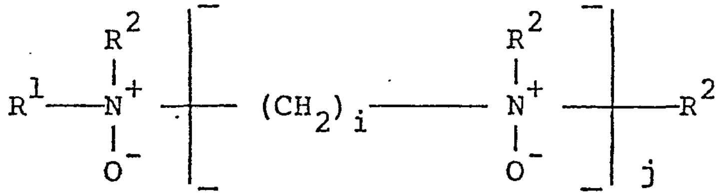
Other useful anionic detergent compounds herein include the water-soluble salts or esters of α-sulphonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulphonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulphates containing from about 10 to 18, especially about 12 to 16, carbon atoms in the alkyl group and from about 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulphonates containing from about 12 to 24, preferably aout 14 to 16, carbon atoms, especially those made by reaction with sulphur trioxide followed by neutralization under conditions such that any sultones present are hydrolysed to the corresponding hydroxy alkane sulphonates; water-soluble salts of paraffin sulphonates containing from about 8 to 24, especially 14 to 18 carbon atoms, and β-alkyloxy alkane sulphonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred. Suitable fatty acid soaps can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24, preferably from about 10 to about 22 and especially from about 16 to about 22 carbon atoms in the alkyl chain. Suitable fatty acids can be obtained from natural sources such as, for instance, from soybean oil, castor oil, tallow, whale and fish oils, grease, lard and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Napthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulfonate and sulfate surfactants in a weight ratio of from about 5:1 to about 1:5, preferably from about 5:1 to about 1:1, more preferably from about 5:1 to about 1.5:1. Especially preferred is a mixture of an alkyl benzene sulfonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal preferably sodium; and either an alkyl sulfate having from 10 to 20, preferably 12 to 18 carbon atoms in the alkyl radical or an ethoxy sulfate having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6, having an alkali metal cation, preferably sodium.

In addition to the above anionic and ethoxylated nonionic surfactants, detergent compositions of the invention can be supplemented by low levels, preferably up to about 6%, of cosurfactants, especially amine oxides, quaternary ammonium surfactants and mixtures thereof.

Suitable surfactants of the amine oxide class have the general formula VIII



$$R^1-\overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle O^-}{|}}{N^+}}-\left[(CH_2)_i-\overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle O^-}{|}}{N^+}}\right]_j-R^2$$

VIII

wherein R^1 is a linear or branched alkyl or alkenyl group having 8 to 20 carbon atoms, each R^2 is independently selected from C_{1-4} alkyl and $-(C_nH_{2n}O)_mH$ where i is an integer from 1 to 6, j is 0 or 1, n is 2 or 3 and m is from 1 to 7, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 7.

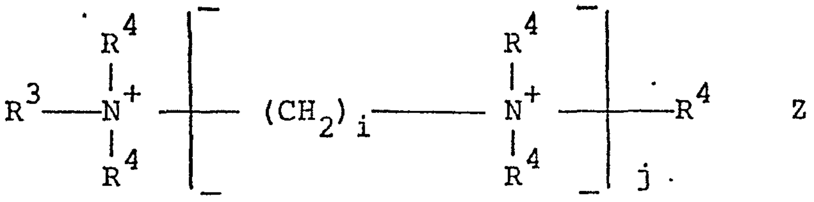
In a preferred embodiment R^1 has from 10 to 14 carbon atoms and each R^2 is independently selected from methyl and $-(C_nH_{2n}O)_mH$ wherein m is from 1 to 3 and the sum total of $C_nH_{2n}O$ groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment, j is 0 and each R^2 is methyl, and R^1 is C_{12}-C_{14} alkyl.

Another suitable class of amine oxide species is represented by bis-amine oxides having the following substituents.

j : 1
R^1: tallow C_{16}-C_{18} alkyl; palmityl; oleyl; stearyl
R_2: hydroxyethyl
i : 2 or 3

A specific example of this preferred class of bis-amine oxides is: N-hydrogenated C_{16}-C_{18} tallow alkyl-N,N',N'tri-(2-hydroxyethyl) -propylene-1,3-diamine oxide.

Suitable quaternary ammonium surfactants for use in the present composition can be defined by the general formula IX:



IX

$$R^3-\overset{R^4}{\underset{R^4}{N^+}}\left[-(CH_2)_i-\overset{R^4}{\underset{R^4}{N^+}}-\right]_j-R^4 \qquad Z$$

wherein R^3 is a linear or branched alkyl, alkenyl or alkaryl group having 8 to 16 carbon atoms and each R^4 is independently selected from C_{1-4} alkyl, C_{1-4} alkaryl and $-(C_nH_{2n}O)_m$ wherein i is an integer from 1 to 6, j is 0 or 1, n is 2 or 3 and m is from 1 to 7, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 7, and wherein Z represents counteranion in number to give electrical neutrality,

In a preferred embodiment, R^3 has from 10 to 14 carbon atoms and each R^4 is independently selected from methyl and $(C_nH_{2n}O)_mH$ wherein m is from 1 to 3 and the sum total of $C_nH_{2n}O$ groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment j is 0, R^4 is selected from methyl, hydroxyethyl and hydroxypropyl and R^3 is C_{12}-C_{14} alkyl. Particularly preferred surfactants of this class include C_{12} alkyl trimethylammonium salts, C_{14} alkyltrimethylammonium salts, coconutalkyltrimethylammonium salts, coconutalkyldimethylhydroxyethylammonium salts, coconutalkyldimethylhydroxypropylammonium salts, and C_{12} alkyldihydroxyethylmethyl ammonium salts.

Another group of useful cationic compounds are the diammonium salts of formula II in which j is 1, R^3 is C_{12}-C_{14} alkyl, each R^4 is methyl, hydroxyethyl or hydroxypropyl and i is 2 or 3. In a particularly preferred surfactant of this type, R^3 is coconut alkyl, R^4 is methyl and i is 3.

Detergent compositions of the invention, particularly those in granular form, can also include at least one detergent organic or inorganic builder salt which can be any one of the water soluble or water insoluble salts conventionally used for this purpose. Suitable inorganic builder salts include orthophosphates, pyrophosphates, tripolyphosphates and the higher polymeric glassy phosphates, silicates, carbonates, and the water insoluble crystalline aluminosilicates such as hydrated Zeolite A, X or P. Organic builder salts include the aminocarboxylates such as the salts of nitrilotriacetic acid (NTA), ethylenediaminetetra acetic acid (EDTA) and diethylenetriaminepenta acetic acid (DETPA) and the methylene phosphonate analogues of these materials nitrilotrimethylene-phosphonic acid (NTMP), ethylendiaminetetramethylenephosphonic acid (EDTMP) and diethylenetriaminepentamethylenephosphonic acid (DETPMP), as well as the salts of polycarboxylic acids such as lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Patents 821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tri-carboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclo-pentane-cis, cis, cis-tetracarboxylic acid; cyclopentadienide pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent 1,425,343.

The builder salts preferably comprise from about 5% to about 96% by weight of the composition, preferably from about

10% to about 50% by weight for granular detergents, and preferably from about 5% to about 20% for liquid detergents.

The compositions of the present invention can be supplemented by all manner of detergent components. Soil suspending agents at about 0.1% to 10% by weight such as water-soluble salts of carboxymethyl-cellulose, carboxyhydroxymethyl cellulose, and polyethylene glycols having a molecular weight of about 400 to 10,000 are common components of the present invention. Dyes, pigments, optical brighteners, and perfumes can be added in varying amounts as desired.

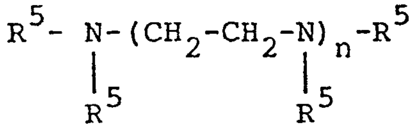
Other materials such as fluorescers, enzymes in minor amounts, anti-caking agents such as sodium sulfosuccinate, and sodium benzoate can also be added. Enzymes suitable for use herein include those discussed in U.S. patents 3,519,570 and 3,533,139 to McCarty and McCarty et al issued July 7 1970 and January 5, 1971 respectively.

An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate preferably is used in an amount from 0.5% to 10% preferably from 3% to 8%. Suitable silicate solids have a molar ratio of SiO_2/alkali $metal_2O$ in the range from about 0.5 to about 4.0, but much more preferably from 1.0 to 1.8, especially about 1.6. The alkali metal silicates suitable herein can be commercial preparations of the combination of silicon dioxide and alkali metal oxide, fused together in varying proportions.

Granular detergent compositions herein can also advantageously contain a peroxy bleaching component in an amount from about 3% to about 40% by weight, preferably from about 8% to about 33% by weight. Examples of suitable peroxy bleach components for use herein include perborates, persulfates, persilicates, perphosphates, percarbonates, and more generally all inorganic and organic peroxy bleaching agents which are known to be adapted for use in the subject compositions. The composition can also advantageously include a bleach activator which is normally an organic compound containing and N-acyl, or an O-acyl (preferably acetyl) group. Preferred materials are N,N,N',N'-tetraacetyl ethylene diamine and N,N,N',N'-tetraacetylglycouril. The bleach activator is preferably added at a level from 0.5% to 5% by weight of composition.

A further preferred ingredient of the instant compositions is from about 0.01 to about 4%, especially from about 0.1 to about 1.0% by weight of a polyphosphonic acid or salt thereof which is found to provide bleachable stain detergency benefits.

Especially preferred polyphosphonates have the formula X:-



$$R^5-\underset{\substack{|\\ R^5}}{N}-(CH_2-CH_2-\underset{\substack{|\\ R^5}}{N})_n-R^5 \qquad X$$

wheren each R^5 is $CH_2PO_3H_2$ or a water-soluble salt thereof and n is from 0 to 2. Examples of compounds within this class are aminotri(methylenephosphonic acid), ethylene diaminetetra(methylenephosphonic acid) and diethylene triaminepenta(methylenephosphonic acid). Of these, ethylenediaminetetra(methylenephosphonic acid) is particularly preferred.

A further optional component is from about 0.1% to about 3%, especially from about 0.25% to about 1.5% of a polymeric material having a molecular weight of from about 2000 to about 2,000,000 and which is a copolymer of maleic acid or anhydride and a polymerisable monomer selected from C_1-C_{12}alkyl vinyl ethers, acrylic and methacrylic acid and C_1-C_{20} esters thereof, alkenes having from 2 to 12 carbon atoms, N-vinyl pyrrolidone and styrene. Highly preferred examples of such carboxylates are 1:1 styrene/maleic acid copolymer, di-isobutylene/maleic acid copolymers, methyl vinyl ether/ maleic acid copolymers of molecular weight from about 50,000 to about 300,000, and 1:1 to 1:4 maleic acid/acrylic acid copolymers of molecular weight from about 12,000 to about 100,000. Other suitable polycarboxylates are poly-α-hydroxy acrylates and lactones thereof as described in Belgian Patent 817,678 and British Patent 1,425,307.

Another suitable component of the present compositions is a water-soluble magnesium salt which is added at levels in the range from about 0.015% to about 0.2%, preferably from about 0.03% to about 0.15% and more preferably from about 0.05% to about 0.12% by weight of the compositions (based on weight of magnesium). Suitable magnesium salts include magnesium sulfate, magnesium sulfate heptahydrate, magnesium chloride, magnesium chloride hexahydrate, magnesium fluoride and magnesium acetate. Desirably, the magnesium salt is added to granular compositions as part of the aqueous slurry crutcher mix and is then converted to dry granular form, for instance by spray drying.

Liquid detergent compositions of the invention can additionally be supplemented by pH regulators such as potassium hydroxide, potassium carbonate, potassium bicarbonate, sodium hydroxide, sodium carbonate, sodium bicarbonate, and mono-, di- and triethanolamine; solvents such as ethyl alcohol, isopropanol, propylene glycol, propane-1, 2-diol, hexyleneglycol; and hydrotropes such as urea.

Granular detergent compositions of the invention are preferably prepared by spray-drying an aqueous slurry comprising the anionic surfactant and detergency builder. The aqueous slurry is mixed at a temperature in the range from about 70-90°C and the water-content of the slurry adjusted to a range of about 25% to about 45%, preferably about 30% to about 38% by weight. Spray drying is undertaken with a drying gas inlet temperature of from about 250-350°C, preferably about 275-330°C, providing a final moisture content in the range of from about 8% to 14% by weight. The dispersion (a) is sprayed in fluid form onto the spray-dried detergent granules and finally dispersion (b) is dry mixed in the composition in powder form.

The granular compositions of the invention can also be prepared in concentrated form with a bulk density greater than about 600 g/litre. A preferred process for preparing a concentrated granule comprises the steps of:

(a) spray drying an aqueous slurry containing anionic surfactant and at least one builder salt to form spray dried carrier granules having a bulk density of at least 450 g/litre and a porosity of at least 0.20 ml/g;

(b) forming base granules having a bulk density of at least 550 g/litre by treating said carrier granules with a fluid spray of dispersion (a) in an amount comprising at least 50% by weight of the nonionic surfactant in the product, and optionally comminuting the base granules;

(c) forming free flowing bleach granules having a bulk density of at least 650 g/litre by treating a particulate inorganic bleach with a fluid spray of dispersion (a) in an amount comprising not more than 50% by weight of the nonionic surfactant in the product; and

(d) blending said bleach granules and said base granules and dispersion (b) in powder form to form a detergent product having a bulk density of at least 600 g/litre.

In the Examples which follow, the abbreviations used have the following designation:-

LAS : Linear $C_{11.8}$ alkyl benzene sulphonate.

TAE(n) : Hardened tallow alcohol ethoxylated with n moles of ethylene oxide.

MAO : C_{12}-C_{14} alkyl dimethylamine oxide.

TAS : Tallow alcohol sulfate.

CATAB : Coconut alkyl trimethyl ammonium bromide.

Dobanol 45-E-7 : A C_{14-15} oxo-alcohol with 7 moles of ethylene oxide, marketed by Shell.

TAED : Tetraacetyl ethylene diamine.

Silicate : Sodium silicate having an $SiO_2:Na_2O$ ratio of 1.6:1.

Wax : Microcrystalline wax - Witcodur 272 M.pt 87°C.

Gantrez AN119 : Trade Name for maleic anhydride/vinyl methyl ether co-polymer, believed to have an average molecular weight of about 240,000, marketed by GAF. This was prehydrolysed with NaOH before addition.

MA/AA : Copolymer of 1:4 maleic acid/acrylic acid, average molecular weight about 80,000.

Brightener : Disodium 4,4'-bis(2-morpholino-4-anilino-s-triazino-6-ylamino)stilbene-2:2'-disulphonate.

Dequest 2060 : Trade Name for diethylenetriaminepenta(methylenephosphonic acid), marketed by Monsanto.

Dequest 2041 : Trade Name for ethylenediamine tetra(methylene phosphonic acid)monohydrate, marketed by Monsanto.

DC 544 : Commercial mixture of alkoxylated siloxane, siloxane liquid, siloxane resin and aerogel silica, marketed by Dow Corning.

DC 198 : Alkoxylated siloxane containing oxyethylene and oxypropylene groups, marketed by Dow Corning.

DC 200 : Polydimethylsiloxane fluid, marketed by Dow Corning.

Silicone/Silica : 85:15 by weight mixture of polydimethylsiloxane and silanated silica.

Silica : Trimethylsilanated silica, particle size 10 to 20 millimicrons.

The present invention is illustrated by the following non-limiting examples:-

EXAMPLES I TO V

Granular detergent compositions are prepared as follows. A base powder composition is first prepared by mixing the indicated components in a crutcher as an aqueous slurry at a temperature of about 80°C and containing about 35% water. The slurry is then spray dried at a gas inlet temperature of about 300°C to form base powder granules. Additive dispersion (a) is then prepared as a molten mixture of the nonionic surfactant, foam-controlling agent and dispersing agent and the mixture is subjected to high shear mixing. Additive dispersion (b) is then formed by dispersing foam controlling agent in molten organic carrier and the dispersion is sprayed onto sodium tripolyphosphate in a fluidized bed. Finally, the base powder composition is dry mixed with additive dispersion (b), enzyme and bleach components, and additive dispersion (a) is sprayed onto the total mixture.

All percentages are given by weight of total detergent composition.

	EXAMPLES				
	I	II	III	IV	V
BASE POWDER					
LAS	7	4	8	12	5
TAS	3	2	2	-	-
MAO	-	-	-	1	1
CATAB	-	1	-	1	-
Gantrez AN119	-	1	-	0.8	1
Silicate	6	7	5	5	10
MA/AA	0.5	-	1	0.4	-
Brightener	0.2	0.3	0.1	0.5	0.2
Dequest 2060	-	-	0.3	0.2	-
Dequest 2041	0.1	0.3	-	-	0.1
EDTA	0.2	0.3	-	0.1	0.2
Sodium tripolyphosphate	32	24	28	32	30
Magnesium sulphate (ppm)	1000	-	800	-	1200
Sodium sulphate, moisture & miscellaneous	——— to 100 ———				

EXAMPLES (continued)

	I	II	III	IV	V
ADDITIVE (a)					
Dobanol 45-E-7	6	10	8	2	12
DC-200	0.2	0.32	0.24	0.1	0.42
DC-198	0.025	0.033	-	0.015	-
DC-544	-	-	0.04	-	0.07
Silicone/silica	-	0.07	-	-	-
ADDITIVE (b)					
TAE(25)	0.28	0.48	0.15	-	-
TAE(80)	-	-	-	0.65	0.18
PEG 6000	-	-	0.15	-	-
Wax	0.03	0.3	-	0.42	0.025
Silica	-	0.027	0.01	0.03	-
Silicone/silica	0.06	-	-	0.04	0.05
DC200	0.13	-	0.14	-	0.1
Sodium tripolyphosphate	1.2	1.9	1.3	2.4	1.0
OTHER ADDITIVES					
Enzyme	0.6	-	1.2	-	0.9
Sodium perborate tetrahydrate	20	12	15	28	22
TAED	-	2	1	-	-

The above products combine superior detergency performance together with excellent foam regulation characteristics across the range of wash temperature, product usage, soil, load and rinsing conditions, even after prolonged storage under warm humid conditions.

CLAIMS

1. A detergent additive composition characterized by:

(a) a dispersion of polydimethylsiloxane foam-controlling agent in an ethoxylated nonionic surfactant, the nonionic surfactant having a hydrophilic- lipophilic balance (HLB) in the range from 9 to 13 and a melting point in the range from 5°C to 36°C, wherein the weight ratio of nonionic surfactant to polydimethylsiloxane is in the range from 10:1 to 100 to 1, and

(b) a dispersion of hydrophobic silica foam-controlling agent in a water-soluble or water-dispersible organic carrier having a melting point in the range from 38°C to 90°C, wherein the weight ratio of organic carrier to hydrophobic silica is in the range from 10:1 to 100:1,

and wherein the weight ratio of dispersion (a) to dispersion (b) is in the range from 1:1 to 50:1.

2. A composition according to Claim 1 characterized in that the organic carrier comprises a second ethoxylated nonionic surfactant, the second nonionic surfactant having an HLB in the range from 13.5 to 19 and a melting point in the range from 38°C to 60°C.

3. A composition according to Claim 1 or 2 characterized in that dispersion (a) additionally comprises hydrophobic silica foam controlling agent, and wherein the weight ratio of hydrophobic silica foam controlling agent in dispersion (b) to that in dispersion (a) is greater than about 1:2.

4. A composition according to Claims 1 to 3 characterized in that dispersion (b) additionally comprises polydimethylsiloxane foam controlling agent, and wherein the weight ratio of polydimethylsiloxane foam-controlling agent in dispersion (b) to that in dispersion (a) is less than about 10:1.

5. A composition according to any of Claims 1 to 4 characterized in that in dispersion (a) the weight ratio of nonionic surfactant to polydimethylsiloxane is in the range from about 15:1 to about 40:1, and in dispersion (b), the weight ratio of organic carrier to hydrophobic silica is in the range from about 15:1 to about 50:1.

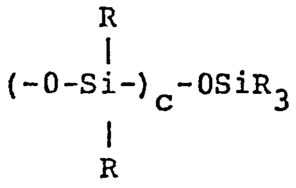
6. A composition according to any of Claims 1 to 5 characterized in that dispersion (a) additionally comprises a siloxane-oxyalkylene copolymer dispersing agent having the general formula I

$$R_aSiY_{4-a} \qquad \text{I}$$

wherein a is 0 or an integer from 1 to 3, R is an alkyl group containing from 1 to 30 carbon atoms, or a group of formula II:

$$R'(OR')_bOR'' \qquad \text{II}$$

wherein R' is an alkylene group containing from 1 to 6 carbon atoms, b has a value of from 1 to 100; and R" is a capping group which is selected from hydrogen, alkyl, acyl, aryl, alkaryl, aralkyl or alkenyl groups containing up to 20 carbon atoms, sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate or isocyanate groups, or mixtures thereof; Y is a group having the formula III:-



$$(-O-\underset{R}{\overset{R}{Si}}-)_c-OSiR_3 \qquad III$$

wherein R is as defined above and c has a value from 1 to 200; and wherein at least one R group in the compound has the formula II; and wherein the weight ratio of polydimethylsiloxane foam controlling agent in dispersion

(a) to siloxane-oxyalkylene copolymer dispersing agent is in the range from about 2:1 to about 20:1, preferably from about 5:1 to about 15:1.

7. A composition according to Claim 6 characterized in that the siloxane-oxyalkylene copolymer is selected from copolymers having the general formula IV to VII

$$R'''_aSi[(OSiMe_2)_p(OSiMeG)_qOSiMe_2G]_{4-a} \qquad IV$$

$$R'''_aSi[(OSiMe_2)_p(OSiMeG)_rOSiMe_3]_{4-a} \qquad V$$

$$GMe_2Si(OSiMe_2)_p(OSiMeG)_qOSiMe_2G, \text{ and} \qquad VI$$

$$Me_3Si(OSiMe_2)_p(OSiMeG)_rOSiMe_3 \qquad VII$$

wherein R''' is a C_{1-10} alkyl group, Me is methyl, G is the group of formula II, a has a value of 0 or 1, p has a value of at least 1, q has a value of 0 to 50 and r has a value of 1 to 50.

8. A composition according to any of Claims 1 to 7 characterized in that dispersion (b) additionally comprises microcrystalline wax foam-controlling agent wherein the weight ratio of microcrystalline wax to hydrophobic silica is in the range from about 20:1 to about 1:1, preferably from about 15:1 to about 2:1.

9. A composition according to any of Claims 1 to 8 characterized by a total of from about 1% to about 30% polydimethylsiloxane foam controller and from about 0.005%

to about 2% hydrophobic silica wherein the weight ratio of polydimethylsiloxane foam controller:hydrophobic silica is in the range from about 3:1 to about 100:1, preferably from about 10:1 to about 60:1.

10. A composition according to any of Claims 2 to 9 characterized in that the first nonionic surfactant has an HLB in the range from about 10 to about 12.5 and a melting point in the range from about 10°C to about 28°C, and the second nonionic surfactant has an HLB in the range from about 15 to about 17.5 and a melting point in the range from about 40°C to about 55°C.

11. A detergent composition characterized by from about 3% to about 30% of anionic surfactant and additionally comprising from about 1% to about 30% of a detergent additive composition according to any of Claims 1 to 10 wherein the total level of anionic and ethoxylated nonionic surfactants is in the range from about 12% to about 50%.

12. A granular detergent composition according to Claim 11 characterized by

(i) from about 30% to about 99% of base powder comprising from about 3% to about 30% of anionic surfactant and from about 5% to about 96% of detergency builder,

(ii) from about 0.9% to about 25% of dispersion (a) sprayed in fluent form onto at least part of the base powder, and

(iii) from about 0.1% to about 5% of dispersion (b) dry-mixed in powder form.

13. A composition according to Claim 11 or 12 characterized by from about 5% to about 20% anionic surfactant, from about 3% to about 20% of dispersion (a) and from about 0.3% to about 2% of dispersion (b), and wherein the total level of anionic and ethoxylated nonionic surfactants is in the range from about 14% to about 30%.

European Patent
Office

EUROPEAN SEARCH REPORT

Application number
EP 83 30 1989

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	FR-A-2 328 040 (PROCTER & GAMBLE CO.) * Claims 1, 2, 7-9, 16 * ---	1,6	C 11 D 3/00 C 11 D 3/37
D,Y	EP-A-0 046 342 (PROCTER & GAMBLE CO.) * Claims 1-6 * ---	1,6	
D,A	EP-A-0 008 829 (PROCTER & GAMBLE LTD.) * Claims 1, 2 * ---		
A	DE-A-2 646 057 (PROCTER & GAMBLE CO.) * Claims 1, 8-11 * ---		
A	EP-A-0 013 028 (HENKEL KGaA) * Claims 1, 4 * -----		TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	30-06-1983	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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