(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 085 448**
B2

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of the new patent specification: **10.10.90**

(51) Int. Cl.[5]: **C 11 D 1/86,** C 11 D 1/75, C 11 D 1/62

(21) Application number: **83200064.0**

(22) Date of filing: **17.01.83**

(54) Detergent compositions.

(30) Priority: **25.01.82 GB 8201948**

(43) Date of publication of application:
10.08.83 Bulletin 83/32

(45) Publication of the grant of the patent:
16.10.85 Bulletin 85/42

(45) Mention of the opposition decision:
10.10.90 Bulletin 90/41

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

(56) References cited:
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EP-A-0 008 142
EP-A-0 042 188
EP-A-0 060 003
DE-A-2 648 304
GB-A-1 375 639
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US-A-4 133 779
US-A-4 174 304
US-A-4 264 479

British Standard BS 5610: 1978

The file contains technical information submitted after the application was filed and not included in this specification

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EP 0 085 448 B2

Courier Press, Leamington Spa, England.

Description

Technical field

This invention relates to detergent compositions. In particular, it relates to granular detergent compositions suitable for washing fabrics, clothes etc in automatic washing machines with improved cleaning performance.

Background

Cationic surfactants have been frequently incorporated into detergent compositions of various types. However, the inclusion of such cationic surfactants is generally for the purpose of providing some adjunct fabric care benefit, and not for the purpose of cleaning. For example, certain cationic surfactants have been included in detergent compositions for the purpose of yielding a germicidal or sanitization benefit to washed surfaces, as is disclosed in U.S Patent 2,742,434, Kopp, issued April 17, 1956; U.S. Patent 3,539,520, Cantor et al, issued November 10, 1970; and U.S. Patent 3,965,026, Lancz, issued June 22, 1976. Other cationic surfactants such as ditallowdimethylammonium chloride, have been included in detergent compositions for the purpose of yielding a fabric-softening benefit, as disclosed in U.S. Patent 3,607,763, Salmon et al, issued September 21, 1971; and U.S. Patent 3,644,203, Lamberti et al, issued February 22, 1972. Such components are also disclosed as being included in detergent compositions for the purpose of controlling static, as well as softening laundered fabrics, in U.S. Patent 3,951,879, Wixon, issued April 20, 1976; and U.S. Patent 3,959,157 Inamorato, issued May 25, 1976.

Certain water-soluble cationic surfactants are also known to enhance cleaning performance, especially on greasy and oily soils, when used in combination with nonionic or anionic surfactants, see for instance European Patent Application, Publication No. 225. For optimum grease detergency performance, however, these compositions require relatively high levels of the cationic and nonionic surfactant components in relation to the anionic surfactant level and this can result in a lack of "robustness", particularly in the areas of clay soil detergency and whiteness maintenance, when the compositions are used in multicycle wash-wear treatments in the presence of rinse-added cationic fabric softener. Moreover, the compositions have their greatest effectiveness at medium to high wash temperature (50°C and above); at low wash temperatures (up to about 40°C) on the other hand, the rate of oil removal is greatly reduced and excessively long wash times are required for optimum performance.

The Applicants have now discovered, however, that excellent grease/oil and lipid soil removal performance can be secured simultaneously with good clay soil detergency and whiteness maintenance, under realistic multicycle wash-wear conditions, including low wash temperatures and carry-over of rinse-added softener, by using an anionic surfactant together with a low level of an auxiliary surfactant system consisting of a mixture of a water-soluble cationic surfactant and a semipolar amine-oxide surfactant.

The addition of amine-oxides to detergent compositions is not new of course. Thus U.S. Patents 3,531,526, 4,133,779 and 3,202,714 all relate to detergent compositions employing amine oxides at relatively high levels in a conventional detergent functionality. However, there is apparently no appreciation in the art of the value of low levels of mixed amine-oxide/cationic surfactant systems in improving low temperature cleaning of greasy, oily and lipid soils under realistic multi-cycle wash-rinse-wear conditions.

The invention thus provides granular detergent compositions suitable for heavy duty laundering purposes having improved cleaning performance especially on greasy, oily and lipid soils without detriment to detergency performance on clay soils and without detriment to the soil suspending or fabric whitening characteristics of the compositions, across the range of wash temperatures and under realistic soil, fabric load and multi wash-rinse-wear cycle conditions.

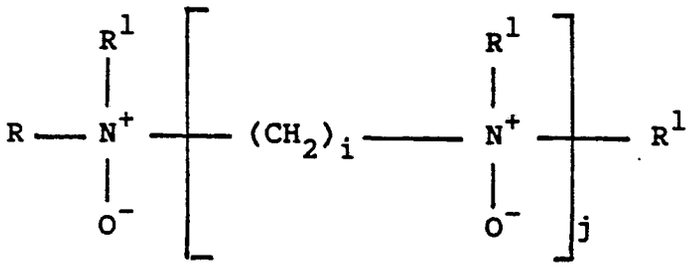
Summary of the invention

According to the present invention, there is provided a granular detergent composition having a pH in 1% by weight aqueous dispersion of at least 7, comprising:

(a) from 2% to 60% by weight of surfactant selected from anionic surfactants and mixtures thereof with nonionic, zwitterionic and ampholytic surfactants;

(b) from 0.5% to 6% by weight of cosurfactant comprising a 5:1 to 1:5 weight ratio mixture of

(i) amine oxide having the general formula I:

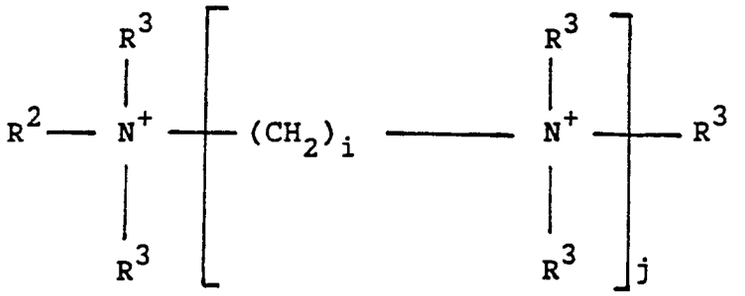


I

wherein R is a linear or branched alkyl or alkenyl group having 10 to 14 carbon atoms, each R^1 is

independently selected from methyl 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 3, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 5, and

(ii) quaternary ammonium surfactant having the general formula II:



II

wherein R^2 is a linear or branched alkyl, alkenyl or alkaryl group having 10 to 14 carbon atoms and each R^3 is independently selected from methyl 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 3, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 5, and wherein Z represents counteranion in number to give electrical neutrality, wherein the weight ratio of surfactant:cosurfactant is at least 1:1 and wherein the equivalent ratio of anionic surfactant:cationic surfactant is also at least 1:1; and

(c) from 5% to 70% by weight of organic or inorganic detergent builder salt.

Detergent compositions of the invention contain a primary surfactant which is an anionic surfactant or a mixture thereof with nonionic, zwiterionic or ampholytic surfactants, and a cosurfactant which is a mixture of water-soluble quaternary ammonium surfactant and amine-oxide. The primary surfactant constitutes from 2% to 60% of the detergent compositions, preferably from 4% to 25%, and especially from 8% to 20%. The auxiliary surfactant system is preferably from 1% to 4% of the detergent composition with the amine oxide and quaternary ammonium surfactants being present at a weight ratio of from 3:1 to 1:3, with the individual cosurfactants each preferably constituting up to 1.5% by weight of composition.

The weight ratio of surfactant:cosurfactant is at least 1:1, preferably from 2:1 to 50:1, more preferably from 3:1 to 20:1. Importantly, the anionic surfactant component is present at an equivalent ratio with respect to the water-soluble quaternary ammonium surfactant of at least 1:1. This is necessary for ensuring optimum grease and lipid soil removal and good suspension of soil in the detergent wash liquor, and for achieving excellent whiteness under multicycle wash-rinse-wear conditions.

Although as discussed above an anionic surfactant is an essential component of the present compositions, preferred compositions contain as the primary surfactant a mixture of anionic and alkoxylated nonionic surfactants in a weight ratio of from 20:1 to 1:5, more preferably from 6:1 to 1:3, especially from 5:1 to 1:1. Such compositions are desirable from the point of view of providing optimum grease, lipid and particulate detergency.

Optimum performance also depends sensitively on the choice of nonionic surfactant and especially desirable from the viewpoint of grease detergency are biodegradable nonionic surfactants have a lower consolute temperature in the range from about 25°C to about 65°C, more preferably from about 30°C to about 50°C. Highly suitable nonionic surfactants of this type have the general formula $RO(CH_2CH_2O)_nH$ wherein R is primary or secondary branched or unbranched C_{9-15} alkyl or alkenyl and n (the average degree of ethoxylation) is from 2 to 9, especially from 3 to 8. More hydrophilic detergents can be employed for providing particulate detergency and anti-redeposition, however, for instance, nonionic detergents of the general formula given above wherein R is primary or secondary, branched or unbranched C_{8-24} alkyl or alkenyl and n is from 10 to 40. Combinations of the two classes of nonionic surfactants can also be used with advantage of course.

The compositions of the invention are formulated to have a pH of at least 7 in the laundry solution at conventional usage concentrations (about 1% by weight) in order to optimize cleaning performance. Granular compositions herein preferably have a pH of from 8.5 to 11.

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

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 US—A—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 about 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 oil, soybean oil, caster 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. Naphthenic 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.

Nonionic surfactants which may be used in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from about 8 to 17, preferably from about 9.5 to 13.5, more 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 30, preferably 5 to 14 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 13 moles of ethylene oxide.

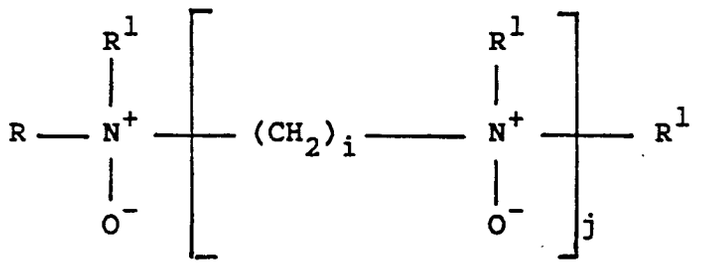
2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 2 to about 40 moles, preferably 2 to about 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises 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 Dobanol 45-4, Dobanol 45-7, Dobanol 45-9, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14, 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.

Also useful are 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 herein 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.

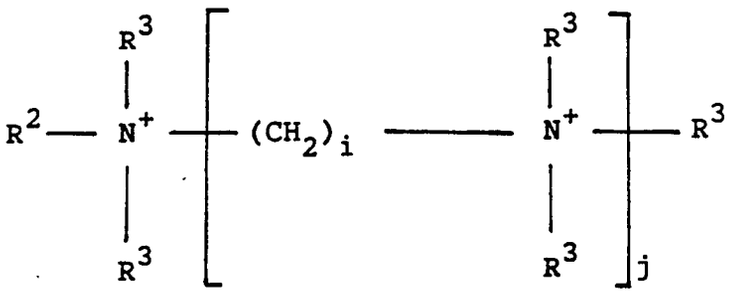
A further essential component of the present compositions is an amine-oxide having the general formula I



I

wherein R is a linear or branched alkyl or alkenyl group having from 10 to 14 carbon atoms and each R^1 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^1 is methyl, and R is C_{12}—C_{14} alkyl.

The quarternary ammonium surfactant component of the present composition is defined by the general formula:



II

Z

wherein R^2 is a linear or branched alkyl, alkenyl or alkaryl group having from 10 to 14 carbon atoms and each R^3 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^3 is selected from methyl, hydroxyethyl and hydroxypropyl and R^2 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} alkyldihydroxyethylmethylammonium salts.

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

The compositions of the invention 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 alumino-silicates 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 NTMP, EDTMP and 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, (ethylene-dioxy) 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 comprise from 5% to 70% by weight of the composition, preferably from 10% to 50% by weight.

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, otpical brighteners, and perfumes can be added in varying amounts as desired.

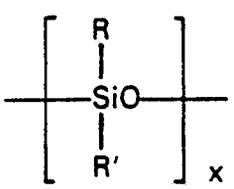
Other materials such as fluorescers, enzymes in minor amounts, anti-caking agents such as sodium sulfosuccinate, and sodium benzoate can also be added. Enzymes suitable for use herein include those discussed in U.S. patents 3,519,570 and 3,533,139 to McCarty and McCarty et al issued July 7, 1970 and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

Anionic fluorescent brightening agents are well-known materials, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostillbene-2:2'-disulphonate disodium 4'4-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethyl-amino)-S-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis-(2-anilino-4-(1-methyl-2-hydroxyethylamino)-S-triazin-6-yl-amino)stilbene-2,2'-disulphonate and sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3-triazole-2''-sulphonate.

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.

The present compositions also contain suds regulating components in an amount of from about 0.05% to about 3%. Preferred are microcrystalline waxes having a melting point in the range from 35°C—115°C and saponification value of less than 100. The microcrystalline waxes are substantially water-insoluble, but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes having a melting point from about 65°C to 100°C, a molecular weight in the range from 400—1000; and a penetration value of at least 6, measured at 77°C by ASTM-D1321. Suitable examples of the above waxes include micro-crystalline and oxidized micro-crystalline petrolatum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax, candelilla; and carnauba wax.

U.S. Patent 3,933,672 issued January 20, 1976, to Bartollota et al., discloses silica suds controlling agent suitable herein. The silicone material can be represented by alkylated polysiloxane materials such as silica aerogens and xerogels and hydrophobic silicas of various types. The silicone material can be described as siloxane having the formula:



wherein X is from about 20 to 2,000 and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl and phenyl. The polydimethylsiloxanes (R and R' are methyl) having a molecular weight within the range of from about 200 to about 2,000,000, and higher, are all useful as suds controlling agents. Additional suitable silicone materials wherein the side chain groups R and R' are alkyl, aryl, or mixed alkyl or aryl hydrocarbyl groups exhibit useful suds controlling properties. Examples of the like ingredients include diethyl-, dipropyl-, dibutyl-, methyl-, ethyl-, phenyl-, methylpolysiloxanes and the like. Additional useful silicone suds controlling agents can be represented by a mixture of an alkylated siloxane, as referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the

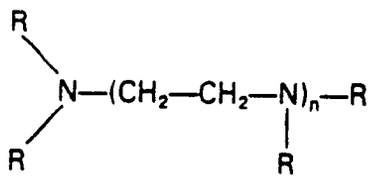
solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from about 10 to 20 nm and a specific surface area above about 50 m^2/g intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:10. The silicone suds suppressing agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier.

Particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in DE—A—2,646,126 published April 28, 1977. An example of such a compound is DB-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

The granular detergent compositions herein can also advantageously contain a peroxy bleaching component in an amount from 3% to 40% by weight, preferably from 8% to 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 an 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—



wherein each R 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 diamine tetra(methylenephosphonic acid) and diethylene triamine penta(methylene phosphonic acid). Of these, ethylenediamine tetra-(methylene phosphonic 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 2000 to 2,000,000 and which is a copolymer of maleic acid 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 and methyl vinyl ether/maleic acid copolymers. Other suitable polycarboxylates are poly-α-hydroxy acrylates and lactones thereof as described in Belgian Patent 817,678 and GB—A—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.

Granular detergent compositions of the invention are preferably prepared by spray-drying an aqueous slurry comprising the primary surfactant, cosurfactant and detergency builder. The aqueous slurry is mixed at a temperature in the range 70—90°C and the water-content of the slurry adjusted to a range of 25% to 45%, preferably 30%—38% by weight. Spray drying is undertaken with drying gas inlet temperature of from about 250—350°C, preferably 275—330°C, providing a final moisture content in the range of from 8% to 14% by weight. Nonionic surfactant, where present, can then be sprayed in fluid form onto the spray-dried detergent granules.

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

LAS:	Linear $C_{11.8}$ alkyl benzene sulphonate.
AS:	Sodium linear C_{12-14} alcohol sulfate.
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.
Silicone Prill:	Comprising 0.14 parts by weight of an 85.15 by weight mixture of silinated silica and silicone granulated with 1.3 parts of sodium tripolyphosphonate, and 0.56 parts of tallow alcohol condensed with 25 molar proportions of ethylene oxide.
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.
Brightener:	Disodium 4,4'-bis(2-morpholino-4-anilino-s-triazino-6-ylamino)stilbene-2,2'-disulphonate.
Dequest® 2060:	Trade Name for diethylenetriamine penta(methylenephosphonic acid), marketed by Monsanto.
Dequest® 2041:	Trade Name for ethylenediamine tetra(methylene phosphonic acid) monohydrate, marketed by Monsanto.

Examples I to IV

Built low-sudsing detergent compositions are prepared having the formulae given below. To make the products a slurry is prepared containing all the components except the nonionic surfactant, silicone prill, bleach and enzyme and the slurry is then spray dried to form a granular intermediate. The bleach and enzyme are then dry-mixed with the grnaular intermediate and the nonionic surfactant is finally sprayed onto the granular mixture. All figures are given as % by weight.

	Examples			
	I	II	III	IV
LAS	—	7	8	—
AS	6	—	—	9
TAS	2	3	4	3
MAO	1	1.5	1.8	1.2
CATAB	1	1.5	1.0	1.8
Dobanol 45-E-7	4	3.2	5	3
Tallowalcohol E-11	1	0.7	1.0	—
TAED	—	—	6	—
Silicate	8	5	1	10
Wax	0.4	0.7	0.5	0.8
Silicone Prill	4	3.3	2	3.5
Gantrez AN119	0.5	0.5	0.5	0.8
Brightener	0.4	0.2	0.2	0.2
Dequest 2060	0.2	—	—	0.1
Dequest 2041	—	0.15	0.4	—
Sodium perborate	25	15	8	18
Alcalase Enzyme	—	0.4	—	—
Sodium tripolyphosphate	30	32	25	35
Magnesium sulfate	—	0.25	0.2	—
Sodium sulfate, moisture and miscellaneous	to 100			

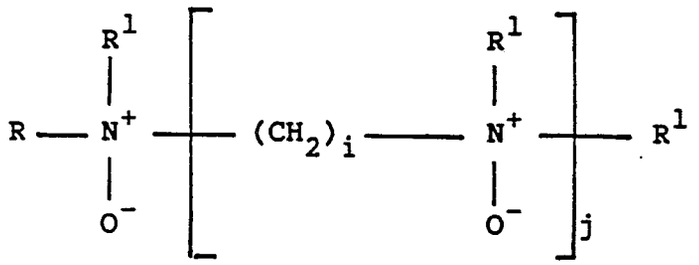
The above products provide excellent grease/oil and lipid soil removal performance simultaneously with good clay soil detergency and whiteness maintenance under realistic multi-cycle wash-wear conditions, including low wash temperatures and carry-over of rinse added softener.

Claims

1. A granular detergent composition having a pH in 1% by weight aqueous dispersion of at least 7, comprising:

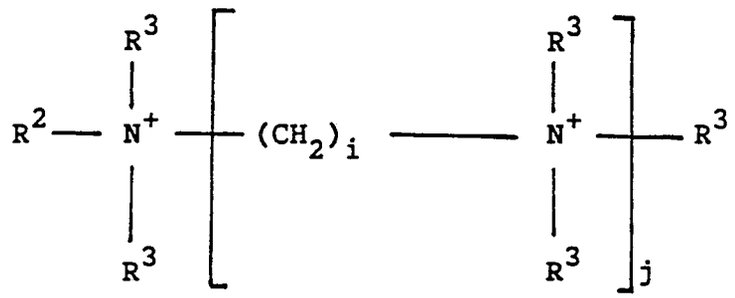
(a) from 2% to 60% by weight of surfactant selected from anionic surfactants and mixtures thereof with nonionic, zwitterionic and ampholytic surfactants;

(b) from 0.5% to 6% by weight of cosurfactant comprising a 5:1 to 1:5 weight ratio mixture of
(i) amine oxide having the general formula I:



I

wherein R is a linear or branched alkyl or alkenyl group having 10 to 14 carbon atoms, each R^1 is independently selected from methyl 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 3, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 5, and
(ii) quaternary ammonium surfactant having the general formula II:



II

wherein R^2 is a linear or branched alkyl, alkenyl or alkaryl group having 10 to 14 carbon atoms and each R^3 is independently selected from methyl 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 3, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 5, and wherein Z represents counteranion in number to give electrical neutrality, wherein the weight ratio of surfactant:cosurfactant is at least 1:1 and wherein the equivalent ratio of anionic surfactant:cationic surfactant is also at least 1:1; and

(c) from 5% to 70% by weight of organic or inorganic detergent builder salt.

2. Composition according to Claim 1 characterized by from 1% to 4% of the cosurfactant system comprising amine oxide and quaternary ammonium surfactant in a weight ratio of from 3:1 to 1:3.

3. Composition according to Claim 1 or 2 characterized in that the weight ratio of surfactant: cosurfactant lies in the range from 2:1 to 50:1, preferably from 3:1 to 20:1.

4. Composition according to any of Claims 1 to 3 characterized in that the surfactant comprises a mixture of anionic and alkoxylated nonionic surfactants in a weight ratio of from 20:1 to 1:5, preferably from 6:1 to 1:3, more preferably from 5:1 to 1:1.

5. A granular detergent composition according to any of Claims 1 to 4 characterized by from 4% to 25% of surfactant, from 1% to 4% of cosurfactant, from 10% to 50% of detergency builder, from 3% to 40% of peroxy bleach and from 0% to 5% of organic peroxyacid bleach activator.

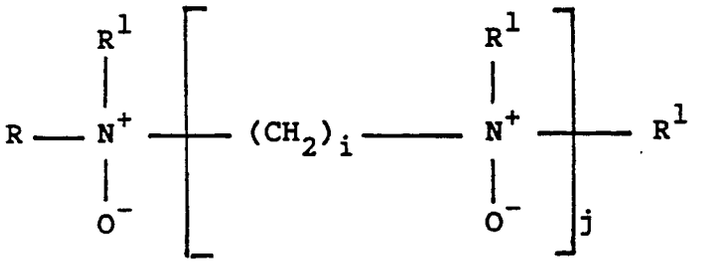
Patentansprüche

1. Granulierte Detergenszusammensetzung mit einem pH-Wert von mindestens 7 in 1 gew.-%iger wäßriger Dispersion, umfassend:

(a) 2 bis 60 Gew.-% an oberflächenaktivem Mittel ausgewählt aus anionischen oberflächenaktiven Mitteln und Gemischen daraus mit nichtionischen, zwitterionischen und ampholytischen oberflächenaktiven Mitteln;

(b) 0,5 bis 6 Gew.-% an mitverwendetem oberflächenaktivem Mittel, umfassend ein Gemisch mit einem Gewichtsverhältnis von 5:1 bis 1:5 aus

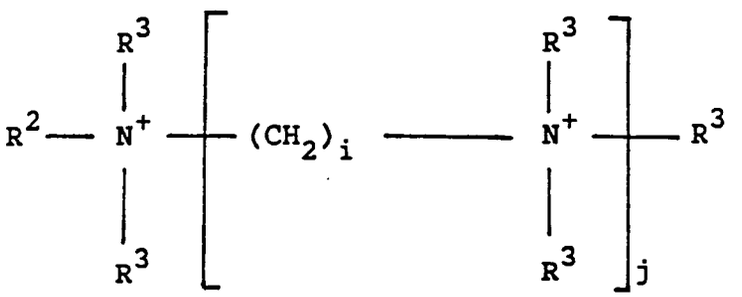
(i) Aminoxid mit der allgemeinen Formel I:



I

worin R eine geradkettige oder verzweigtkettige Alkyl- oder Alkenylgruppe mit 10 bis 14 Kohlenstoffatomen bedeutet, jeder Rest R^1 unabhängig voneinander ausgewählt ist aus Methyl und $-(C_nH_{2n}O)_mH$, wobei i eine ganze Zahl von 1 bis 6 bedeutet, j 0 oder 1 bedeutet, n 2 oder 3 bedeutet und m 1 bis 3 bedeutet, wobei die Gesamtsumme der Gruppen $C_nH_{2n}O$ in einem Molekül nicht mehr als 5 beträgt, und

(ii) einer oberflächenaktiven quaternären Ammoniumverbindung der allgemeinen Formel II:



II

Z

worin R^2 eine geradkettige oder verzweigtkettige Alkyl-, Alkenyl- oder Alkarylgruppe mit 10 bis 14 Kohlenstoffatomen bedeutet und jeder Rest R^3 unabhängig voneinander ausgewählt ist aus Methyl und $-(C_nH_{2n}O)_m$, wobei i eine ganze Zahl von 1 bis 6 bedeutet, j 0 oder 1 bedeutet, n 2 oder 3 bedeutet und m 1 bis 3 bedeutet, wobei die Gesamtsumme der Gruppen $C_nH_{2n}O$ in einem Molekül nicht mehr als 5 beträgt, und wobei Z ein Gegenanion in einer Anzahl, um elektrische Neutralität zu erzielen, darstellt, wobei das Gewichtsverhältnis von oberflächenaktivem Mittel zu mitverwendetem oberflächenaktivem Mittel mindestens 1:1 beträgt und wobei das Äquivalent-verhältnis von anionischem oberflächenaktivem Mittel zu kationischem oberflächenaktivem Mittel ebenfalls mindestens 1:1 beträgt und

(c) 5 bis 70 Gew.% eines organischen oder anorganischen Detergensgerüststoffes.

2. Detergenszusammensetzung gemäß Anspruch 1, gekennzeichnet durch 1 bis 4% an dem System aus mitverwendetem oberflächenaktivem Mittel aus Aminoxid und oberflächenaktiver quaternärer Ammoniumverbindung in einem Gewichtsverhältnis von 3:1 bis 1:3.

3. Zusammensetzung gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Gewichtsverhältnis von oberflächenaktivem Mittel zu mitverwendetem oberflächenaktivem Mittel im Bereich von 2:1 bis 50:1, vorzugsweise von 3:1 bis 20:1, liegt.

4. Zusammensetzung gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das oberflächenaktive Mittel ein Gemisch aus anionischen und alkoxylierten nichtionischen oberflächenaktiven Mitteln in einem Gewichtsverhältnis von 20:1 bis 1:5, vorzugsweise von 6:1 bis 1:3, insbesondere von 5:1 bis 1:1, umfaßt.

5. Granulierte Detergenszusammensetzung gemäß einem der Ansprüche 1 bis 4, gekennzeichnet durch 4 bis 25% oberflächenaktivem Mittel, 1 bis 4% mitverwendetem oberflächenaktivem Mittel, 10 bis 50% Detergensgerüststoff, 3 bis 40% Peroxybleichmittel und 0 bis 5% einer organischen Peroxysäure als Bleichaktivator.

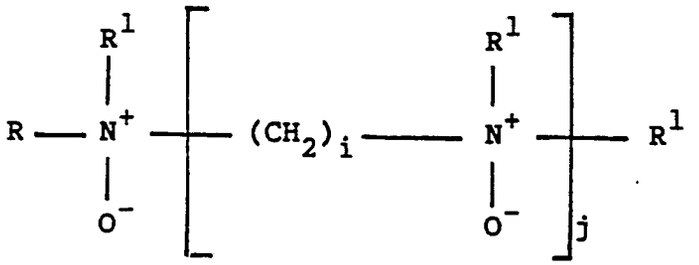
Revendications

1. Composition détergente granulaire ayant, en dispersion aqueuse à 1% en poids, un pH d'au moins 7, comprenant:

(a) de 2% à 60% en poids de tensio-actif choisi parmi les tensio-actifs anioniques et leurs mélanges avec des tensio-actifs non ioniques, de type zwitterion et ampholytes;

(b) de 0,5 à 6% en poids de cotensio-actif comprenant un mélange, selon un rapport pondéral de 5:1 à 1:5, de:

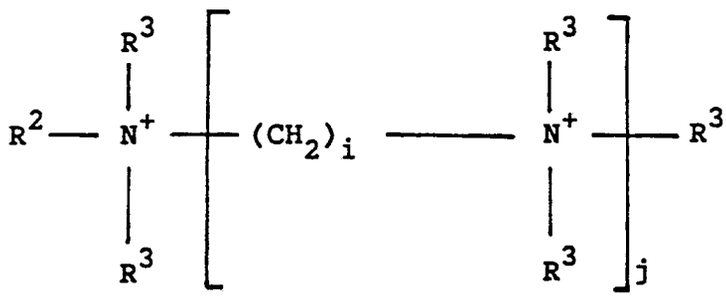
(i) un oxyde d'amine ayant la formule générale I:



I

dans laquelle R est un groupe alkyle ou alkényle linéaire ou ramifié ayant 10 à 14 atomes de carbone, chaque R^1 est choisi, indépendamment, parmi les groupes méthyles et $-(C_nH_{2n}O)_mH$, i est un nombre entier valant de 1 à 6, j vaut 0 ou 1, n est 2 ou 3 et m vaut 1 à 3, la somme totale des groupes $C_nH_{2n}O$ n'étant dans une molécule par supérieure à 5, et

(ii) un tensio-actif de type ammonium quaternaire ayant la formule générale II:



II

Z

dans laquelle R^2 est un groupe alkyle, alcényle ou alcaryle linéaire ou ramifié ayant 10 à 14 atomes de carbone et chaque R^3 est choisi indépendamment parmi un groupe méthyle et $-(C_nH_{2n}O)_m$, i est un nombre entier valant de 1 à 6, j vaut 0 ou 1, n vaut 2 ou 3 et m vaut 1 à 3, la somme totale des groupes $C_nH_{2n}O$ présents dans une molécule n'étant pas supérieure à 5, et Z représente un contre-anion et nombre suffisant pour la neutralité électrique,

le rapport pondéral tensi-actif: cotensio-actif étant au moins égal à 1:1, et la rapport équivalent de tensio-actif anionique:tensio-actif cationique étant aussi au moins égal à 1:1, et

(c) de 5% à 70% en poids d'un sel organique ou minéral adjuvant de détergence.

2. Composition selon la revendication 1, caractérisée en ce que de 1% à 4% du système de cotensi-actif comprend un oxyde d'amine et un tensio-actif de type ammonium quaternaire, selon un rapport pondéral de 3:1 à 1:3.

3. Composition selon la revendication 1 ou 2, caractérisée en ce que le rapport pondéral tensio-actif:cotensio-actif se situe dans l'intervalle allant de 2:1 à 50:1, de préférence de 3:1 à 20:1.

4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le tensio-actif comprend un mélange de tensio-actifs anionique et non ionique alkoxylé, selon un rapport pondéral de 20:1 à 1:5, de préférene de 6:1 à 1:3, encore mieux de 5:1 à 1:1.

5. Composition détergente granulaire selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle comporte de 4 à 25% de ensio-actif, de 1 à 4% de cotensio-actif, de 10% à 50% d'adjuvant de détergence, de 3% à 40% de peroxyde de blanchiment et de 0 à 5% d'un activateur de blanchiment de type peracide organique.