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

(11) Publication number: **0 385 562 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **90300023.0**

(51) Int. Cl.5: **C11D 1/835, C11D 3/42**

(22) Date of filing: **02.01.90**

The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

(30) Priority: **03.01.89 US 292837**

(43) Date of publication of application: **05.09.90 Bulletin 90/36**

(84) Designated Contracting States: **AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

(71) Applicant: **Amway Corporation**
7575 East Fulton Road
Ada Michigan 49355(US)

(72) Inventor: **Brouwer, Steven John**
3466 Golfside Drive
Hudsonville Michigan 49426(US)

(74) Representative: **Robinson, Anthony John Metcalf et al**
Kilburn & Strode 30 John Street
London, WC1N 2DD(GB)

(54) Laundry detergent composition.

(57) Granulated laundry detergents comprising an admixture of at least one builder, at least one fluorescer, at least one nonionic surfactant and at least one cationic surfactant comprising a quaternary ammonium compound in which three of the substituents are lower alkyl or modified alkyl groups and the fourth substituent comprises a long chain alkyl or modified alkyl group joined to the nitrogen atom through an electronegative group. The laundry detergents are effective for removing oily stains with minimal soil redeposition and do not substantially affect the performance of the anionic fluorescers.

EP 0 385 562 A2

NONIONIC LAUNDRY DETERGENT COMPOSITION

This invention relates to granulated laundry detergent compositions comprising a mixture of a nonionic surfactant with a cationic surfactant.

Cationic surfactants have been incorporated into detergent compositions, generally for the purpose of providing some fabric care benefit other than detergency, such as the provision of germicidal and sanitization benefits to washed surfaces, to soften fabrics and to control static.

The use of cationic surfactants in detergent compositions is not without drawbacks. The cationic surfactants complex with anionic detergents and whiteners and precipitate to eliminate the functional characteristics of the anionic and cationic materials. Anionic whitener and brightener compounds are quenched or inhibited in effectiveness in the presence of cationic surfactants. Cationic materials can also be detrimental to soil suspending. Many cationics attract soils to clean fabrics, thus compromising the cleaning ability of the compositions.

Among the approaches taken by detergent artisans to accommodate to the anionic-cationic incompatibility is to provide a composition wherein the surfactant system is substantially neutral with respect to the anionic and cationic material and preferably has an ionic excess of surfactant anions over surfactant cations. Otherwise, the cationic materials have been employed in a separate cycle so as to eliminate contact between the anionic materials and the cationic surfactants.

While compositions comprising mixtures of anionic, cationic and nonionic surfactants are known in the art, laundry detergents comprising a mixture of nonionics and cationics alone are not commonly practical. This is due in no small measure to the extreme difficulty of formulating a properly balanced system. The high level of nonionic and the excess cations with respect to anionic brightener contribute to a reduction in brightness and a greater tendency for soil to become redeposited upon the fabric. Thus, it has been considered necessary to add anionics back to nonionic/cationic combinations to reduce the soil redeposition problem and to inhibit the negative effect of the cationic compound, vis-a-vis the brighteners. However, this approach reduces detergency gains attributed to the cationic surfactant and, thus, results in a compromise between detergency and whitening.

The use of nonionic and cationic mixtures as detergents has thus been limited to special detergent formulations such as degreasers and hard surface cleaners where (1) no whitener is included in the formulations and (2) the cleaning is not accomplished in a closed container, such as a washing machine, with suspended dirt which can be redeposited in the wash.

According to the present invention, a granular laundry detergent comprises at least one nonionic surfactant, at least one anionic whitening agent, at least one builder and at least one cationic surfactant comprising a quaternary ammonium compound in which three of the substituents are lower alkyl or modified lower alkyl groups and the fourth substituent comprises a long chain alkyl or modified alkyl group joined to the nitrogen atom through an electronegative group which diminishes the aggressiveness of the cation towards the brightener and dirt redeposition.

PREFERRED EMBODIMENT

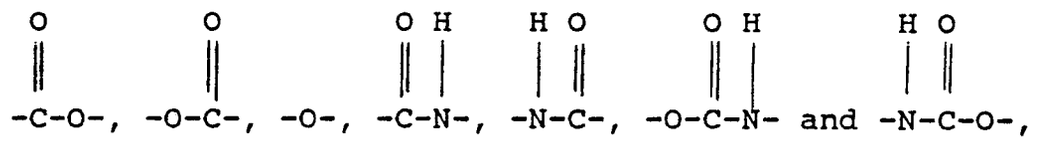
The principal ingredients of the granular laundry detergent of the invention preferably include at least one nonionic surfactant, at least one anionic fluorescer, at least one builder and at least one etheramine-based cationic surfactant as described above. These principal ingredients may be included in the detergent compositions in the following ranges:

Ingredient	Range	Preferred Range	Best Mode
Nonionic Surfactant	7-25	12-20	16
Cationic Surfactant	1-6	2-5	4
Builder	10-75	12.5-75	68
Fluorescer	0.05-1.5	0.25-1.0	0.4
Optionals	to 100%	to 100%	to 100%

The Cationic Surfactant

The quaternary etheramine-based cationic surfactants which are employed in the invention have the general formula $R_1\text{-}E_zR_2R_3R_4N^+X$ wherein R_1 is an alkyl group having from 8 to 24 carbon atoms, preferably 8 to 20 and most preferably 12 to 16 carbon atoms; R_2, R_3 and R_4 are the same or different and each independently is an alkyl group having from 1 to 4 carbon atoms or a hydroxy alkyl radical having the formula $H(OR_5)_x$, wherein R_5 is an alkylene radical having from 1 to 4 carbon atoms and x is an integer in the range from 1 to 4, E is a divalent electronegative group and z is an integer in the range from 1 to 4, with the proviso that at least one of R_2, R_3 or R_4 must be an alkyl group having from 1 to 4 carbon atoms and is preferably methyl.

The electronegative group $(E)_z$ is a divalent radical directly attached to the nitrogen atom through a carbon-nitrogen linkage. The E group can have the formula $-(A(CH_2)_y)_z$, wherein A is selected from the group consisting of



and is preferably -O- and y is an integer in the range from 1 to 8, and is preferably 3, and z is as previously defined. Preferably, the electronegative group E is a divalent radical having the formula $O\text{-}(CH_2R_6)_m$, wherein R_6 is either hydrogen or preferably an alkylene group having from 1 to 4 carbon atoms, most prefera-bly 2 carbon atoms, and m is from 1 to 5, and is preferably 1.

R_1 is a long chain alkyl group having from 8 to 20 carbon atoms which is directly attached through a carbon linkage to the electronegative group. R_1 can be an unbranched chain but is preferably a highly branched alkyl chain having no more than 4 carbon atoms in the longest unbranched group, with isotridecyl being the currently preferred long chain alkyl group.

R_2, R_3 and R_4 can be the same or different and each is independently an alkyl group having from 1 to 4 carbon atoms, preferably methyl and/or $H(OC_nH_2n)_m$ wherein n is 1 to 4 and is preferably 2, and m is 1 to 10 and is preferably 1, with the proviso that at least one of R_2, R_3 and R_4 is an alkyl group of 1 to 4 carbon atoms and is preferably methyl.

Nonionic Surfactants

Substantially any of the nonionic surfactants which have been habitually used in detergent compositions can be employed in the present invention. Representative of such nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having from 1 to 15, preferably 6 to 12 carbon atoms in a straight chain or branch chain configuration with from 4 to 25, preferably 4 to 16 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituents in such compounds can be derived, for example, from polymerized polypropylene, diisobutylene and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecyl phenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630, marketed by the GAF Corporation, and Triton X-45, X-114, X-100 and X-102, all marketed by the Rohm and Haas Company. Igepal and Triton are trade marks.

2. The condensation products of aliphatic alcohols with from 1 to 25, and preferably 5 to 16 moles of ethylene oxide. The alkyl chain with the aliphatic alcohol can either be straight or branched, primary or secondary and generally contains from about 8 to 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation products of myristyl alcohol condensed with about 10 moles of ethylene oxide per

mole of alcohol; and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms). Examples of commercially available nonionic surfactants of this type include Tergitol 15-S-9, marketed by Union Carbide Corporation; Neodol 45-9, Neodol 23-6.5, Neodol 45-7 and Neodol 25-7, marketed by Shell Chemical Company and KYRO EOB, marketed by the Proctor & Gamble Company. The ethoxylated alcohols are currently preferred nonionic surfactants. Tergitol, Neodol and KYRO are trade marks.

3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds has a molecular weight from about 1,500 to 1,800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation of up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available PLURONIC surfactants, marketed by Wyandot Chemical Corporation. PLURONIC is a trade mark.

4. The condensation products of ethylene oxide with a product resulting from the reaction of propylene oxide and ethylene diamine. The hydrophobic moiety of these products consists of the reaction product of ethylene diamine and excess propylene oxide, the moiety having a molecular weight from about 2,500 to 3,000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TECTRONIC compounds marketed by Wyandot Chemical Corporation. TECTRONIC is a trade mark.

5. Semi-polar nonionic detergent surfactants which include water-soluble amine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxy alkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety from about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxy alkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxy alkyl moieties of from 1 to 3 carbon atoms.

6. Alkyl polysaccharides having a hydrophobic group containing from 6 to 30 carbon atoms, preferably from 10 to 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.5 to 10, preferably 1.5 to 3, most preferably 1.6 to 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, such as glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. The hydrophobic group can be attached at the 2, 3 or 4 positions thus giving a glucose or galactose as opposed to a glucoside or a galactoside. The intersaccharide bonds can be between the 1 position of the additional saccharide units and the 2-, 3-, 4- and/or 6 positions of the preceding saccharide units. Optionally, and less desirably, there can be a polyalkylene oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkylene oxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to 18, preferably 10 to 16 carbon atoms. Preferably, the alkyl chain group is a straight chain saturated group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkylene oxide chain can obtain up to 10, preferably less than 5, most preferably 0, alkylene oxide moieties. Suitable alkyl polysaccharides are octyl, nonyl decyl, undecyl dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl, di-, tri-, tetra-, penta- and hexaglucosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra- and pentaglucosides and taloalkyl tetra-, penta- and hexaglucosides.

7. Fatty acid amine detergent surfactants having the formula R_7-CO-NR_8R_8, wherein R_7 is an alkyl group containing from 7 to 21, preferably 9 to 17, carbon atoms and each R_8 is hydrogen, an alkyl group having from 1 to 4 carbon atoms, hydroxy alkyl group having from 1 to 4 carbon atoms and $-(C_2H_4O)_nH$ where n is 1 to 3, and is preferably 1.

Whiteners/Brighteners

Substantially any of the known anionic fluorescent brightening and/or whitening agents can be employed in the practice of this invention. Examples of such anionic fluorescers are disodium 4,4′-bis-(2-diethanolamino-4-anilino-s-triazine-6-ylamino)-stilbene-2:2′ disulfonate, disodium 4,4′-bis-(2-morpholino-4-

anilino-s-triazine-6-ylamino)-stilbene-2:2′-disulfonate, disodium 4,4′-bis-(2,4-dianilino-s-triazine-6-ylamino)-stilbene-2:2′-disulfonate, disodium 4,4′-bis-(2-anilino-4-(n-methyl-N-2-hydroxyethylamino)-s-triazine-6-ylamino)-stilbene-2-2′-disulfonate, disodium 4,4′-bis-(4-phenol-2,1,3-trizol-2-yl)-stilbene-2:2′-disulfonate, disodium 4,4′-bis-2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazine-6-ylamino)-stilbene-2:2′-disulfonate and sodium 2(stilbene-4″-(naphtho-1′,2′:4,5)-1,2,3-triazole-2″-sulfonate, diamino stilbene disulphonic acid-cyanuric chloride, distyrylbi-phenyl, naphthotriazoyl stilbene, 7-dimethylamino-4-methylcoumarin, 7-diethylamino-4-methylcoumarin, 4,4′-bis[(4,6-dianilinotriazine-2-yl) amino]-2,2′ stilbene disulfonate acid, 4,4′-bis[(4-anilino-6-bis[(2-hydroxy ethyl) amino]-s-triazine-2-yl) amino]-2,2′ stilbene disulphonic acid, 4,4′-bis[(4-anilino-6-morphilino-s-triazine-2-yl) amino]-2,2′ stilbene disulphonic acid, 4,4′-bis[(4-anilino-6[N-2-hydroxy ethyl-N-methyl amino]-s-triazine-2-yl) amino]-2,2′ stilbene disulphonic acid disodium salt, 4,4′-bis[(4-anilino-6-[(2-hydroxy hydroxyl propyl) amino]-s-triazine-2-yl) amino]-2,2′-stilbene disulphonic acid disodium salt, 2,2-(4,4′-biphenylene divinylene)-dibenzene disulphonic acid disodium salt and 4,[2H-naphthol(1,2-d) triazole-2-yl]-2-stilbene sulphonic acid sodium salt. The currently most preferred whiteners are:

4,4′-bis[(4-anilino-6-[bis(2-hydroxy ethyl) amino]-s-triazine-2-yl) amino]-2,2′ stilbene disulphonic acid, (Industry designation DASC-2)

4,4′-bis[(4-anilino-6-(N-2-hydroxy ethyl-N-methylamino]-s-triazine-2-yl) amino]-2,2′ stilbene disulphonic acid disodium salt (Industry designation DASC-4), and

4-[2H-naphthol(1,2-d) triazole-2-yl]-2-stilbene sulphonic acid sodium salt (Industry designation NTS-1).

Nonionic brighteners, such as p-[3-(p-chlorophenyl)-2-pyrozolin-1-yl] benzenesulfonamide ((Industry designation P-1), can also be incorporated into the granular detergents of the invention.

Builders

The granular detergent compositions of the invention also contain at least 10% of a detergency builder, especially a water-soluble inorganic or organic electrolyte. Suitable electrolytes have an equivalent weight of less than 210, especially less than 100 and include the common alkaline polyvalent calcium ion sequestering agents. The builder can also include water-insoluble calcium ionic exchange materials.

Nonlimiting examples of suitable water-soluble, inorganic detergent builders include alkaline metal carbonates, borates, phosphates, polyphosphates, bicarbonates, silicates, sulphates, and chlorides. Specific examples of such salts include sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, orthophosphates, pyrophosphates, hexametaphosphates and sulphates.

Examples of suitable organic alkaline detergency builders include water-soluble amino carboxylates and amino polyacetates, such as sodium and potassium glycinates, ethylene diamine tetraacetates, nitrilotriacetates and N-(2-hydroxy ethyl) nitrilodiacetates and diethylenetriamine pentaacetates; water-soluble salts of phytic acid, such as sodium and potassium phytates; water-soluble polyphosphonates including sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid, the sodium potassium and lithium salts of ethylene diphosphonic acid and the like; water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethyloxysuccinic acid, 2-oxo-xa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, cylcopentane-cis,cis,cis-tetracarboxylic acid mellitic acid and pyromellitic acid; water-soluble organic amines and amine salts such as monoethanolamine, diethanolamine and triethanolamine and salts thereof.

Another type of detergency builder useful in the present composition comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates, especially those having a calcium ionic exchange capacity of at least 200 milligrams equivalent per gram and a calcium ion exchange rate of at least 2 grams per gallon per minute per gram.

Additional Ingredients

The granular detergent compositions of the present invention can be supplemented by the usual additives conventionally employed in detergent compositions. Optional ingredients may include soil suspending agents at about 0.1% to 10% by weight, including water-soluble salts of carboxy-methylcellulose carboxyhydroxymethyl-cellulose and poly-ethylene glycols having a molecular weight of about 400 to

10,000. Dyes, pigment optical brighteners and perfumes, enzymes, anti-caking agents such as sodium sulfosuccinate, preservatives such as sodium benzoate, alkaline metal or alkaline earth metal silicates, suds regulating or suppressing agents, natural and synthetic microcrystalline and oxidized microcrystalline waxes, inorganic and organic peroxy bleaching agents, polyphosphonic acids and acid salts. These materials will be employed in the practice of this invention at conventional levels normally employed in detergent formulations.

Use And Manufacture

The granular detergent compositions of this invention are typically employed in an amount to provide aqueous solutions containing from about 100 to about 3,000 parts per million, especially from about 500 to 1,500 parts per million of detergent compositions.

The detergent compositions of the invention are prepared following conventional techniques. For example, the granular detergent compositions of the present invention can be made by spray drying a crutcher mix containing the brightener, cationic surfactant and builder components and subsequently absorbing the nonionic surfactant in liquid or molten form into the spray-dried granules. This method is particularly valuable when the builder comprises an aluminosilicate ion-exchange material.

In a variation of this method wherein the detergent compositions comprise an aluminosilicate builder, the nonionic is included in the crutcher mix for spray drying, but the components of the surfactants are premixed before addition of the aluminosilicate builder.

In another method, the brightener, builder and optional components can be spray dried in conventional manner to form a base powder composition and the quaternary ammonium cationic surfactant can then be added to the base powder either as an approximately 1:1 mixture with part of the builder or filler components retained for that purpose, or as an inclusion complex of, for instance, urea. Alternatively, the cationic surfactant can be sprayed onto the base powder, or added as a dry mixed prill agglomerated with an inorganic or organic agglomerating aid, or can be separately spray dried and added to the base powder as a dried mixed granule. Alternatively, the cationic surfactant and base powder compositions can be individually spray dried in separate stages of a multi-stage spray drying tower.

Currently, the preferred method of preparing the granular laundry detergent is to blend the dry powdery ingredients, such as builder, fluorescer, anticaking agents and the like, to obtain a substantially homogenous mixture. Liquid materials, such as the nonionic and cationic surfactants, are then blended into the dry mixture to provide a dampened powder composition. The dampened powder is then sprayed with a liquid agglomerating agent, such as sodium silicate.

Best Mode Formulation

Ingredient	General Range	Preferred Range	Best Mode
Sodium tripolyphosphate	0.0-75.0	2-75	47.5
Sodium carbonate	10.0-75.0	10-75	20.36
Fluorescent whitening agent, Tinopal UNPA	0.05-1.5	0.1-1.0	0.35
Fluorescent whitening agent, Phorwite FBW	0.01-1.5	0.02-1.0	0.04
Carboxymethylcellulose	1.60	1.60	1.60
Nonionic surfactant	7.00-25.00	12.00-20.00	16.00
Quaternary ammonium cationic surfactant	1.00-6.00	2.00-5.00	4.00
Fragrance	0.15	0.15	0.15
Soft water	4.5	4.5	4.5
Sodium hydroxide solution, 50%	1.0	1.0	1.0
Liquid sodium silicate	4.0	4.0	4.0
Enzymes	0.5	0.5	0.5

The nonionic surfactant used in the best mode is Pareth 2-7, available from Shell Chemical under the trademark Neodol 25-7. The quaternary ammonium cationic surfactant used in the best mode is isotridecyloxypropyl-bis(2-hydroxyethyl)methylammonium chloride, available from Exxon under the trade-

mark Tomah Q-17-2. The whitener used in the best mode is DASC-2, available from Ciba Geigy under the trademark Tinopal UNPA-GX.

Experimental Procedures And Results

The detergent compositions were evaluated in the examples as follows:

Soiled cloths were washed in a laboratory-scale washing machine (Terg-O-Tometer, U.S. Testing Company) which simulates the action of an agitator-type home washer. Appropriate amounts of detergent formulations are added to one litre of water at a controlled hardness. Wash temperature, agitator speed and wash, as well as rinse, time can be controlled via the Terg-O-Tometer. After washing, rinsing (machine or by hand) and drying, detergency is taken as a change in the reflectance of the cloths. Assignments of formulas to the test spots are randomized using a simple random number table.

The effectiveness of the detergent compositions is determined by reflectance readings using a Gardner Color Difference Meter, with all cloths being read before and after laundering. Each cloth is individually placed on the reflectometer and covered by a white ceramic plate standard. For the Bandy black clay soil cloths, only Rd readings are taken. For all cloths, a and b values, in addition to Rd readings, may be observed. The reflectometer uses Rd, a and b readings to calculate whiteness index (WI).

The soil types which were evaluated are as follows:

Bandy Black Clay: an artificially prepared soil cloth prepared by a dry soiling method where the clay is ball milled into the fabric.

TFI: a printed soil cloth (mineral oil-carbon black base) purchased from Test Fabrics Incorporated.

HCO: a soiled cloth prepared by immersion in a lard, margarine and peanut oil-carbon black mixture.

Grass: a soiled cloth prepared by immersion in an aqueous solution of freshly cut grass.

Spangler: a soiled cloth prepared by immersion in a soil bath (synthetic sebum, air conditioner dust) and then padded and dried.

EMPA: a soiled cloth prepared by immersion in an olive oil-carbon black mixture.

DMO: a soiled cloth prepared by immersion in dirty motor oil.

Cotton, cotton/Dacron, cotton with finish, cotton: Dacron with finish were used for the Bandy Black Clay, TFI, grass, DMO, HCO and Spangler soils. Cotton and cotton:Dacron with finish were used for EMPA soil.

In the following examples, the detergent compositions were prepared by mechanically blending dry powdery ingredients, blending in the liquid components and spraying the resulting damp powdery composition with liquid sodium silicate agglomerating material. In each example, the formulations for the various detergents tested are indicated at the top of the table.

All examples contain the following ingredients in the amounts indicated:

Ingredients	Parts By Weight (PBW)
Sodium Tripolyphosphate	47.50
Sodium Carbonate	21.90
Carboxymethylcellulose	1.60
Fragrance	0.15
Sodium Hydroxide	0.50
Sodium Silicate	14.00
Enzyme	0.50
Total	86.15

These common ingredients will be hereinafter referred to as the Basic Formulation to which will be added fluorescers, nonionic surfactants, cationic surfactants and anionic surfactants. The cationic surfactants will include both quaternary ammonium cationic surfactants which are encompassed by the inventive concept herein and quaternary ammonium cationic surfactants which are not encompassed by the inventive concepts herein. The use of these latter cationic surfactants is for comparison purposes.

In the examples, the abbreviations used have the following designations:

Fluorescent Whitening Agents

DASC-2: 4,4′-bis [(4-anilino-6-[bis(2--hydroxyethyl) amino]-s-triazi-ne-2-yl)amino]-2,2′-stilbene disulphonic acid.
DASC-4: 4,4′-bis[(4-anilino-6-[N-2--hydroxyethyl-N-methyla-mino]-s-triazine-2-yl)-amino]-2,2′-stilbene disulphonic acid disodium salt.
NTS-1: 4-[2H-naphtol(1,2-d) triazole-2-yl]--2-stilbene sulphonic acid sodium salt.

Nonionic Surfactants

Pareth 25-7: C_{12-15} ethoxylate with 7 moles of ethylene oxide.
Pareth 25-3: C_{12-15} ethoxylate with 3 moles ethylene oxide.
712: Tertiary C_{12} thioethylate with 7 moles ethylene oxide.
AO: Isotridecyloxypropylbis(2-hydroxyethyl)amine oxide.

Quaternary Ammonium Cationic Surfactants Within the Scope of the Invention:

Incat 1: Isotridecyloxypropylbis(2-hydroxyethyl)methylammonium chloride
Incat 2: Isododecyloxypropylbis(2-hydroxyethyl)methylammonium chloride
Incat 3: Isodecyloxypropylbis(2-hydroxyethyl)methylammonium chloride
Incat 4: N-(branched) C_{19} alkyloxypropylbis(2--hydroxyethyl)methylammonium chloride
Incat 5: C_{12-15} linear alkyloxypropylbis(2-hydroxyethyl)methylammonium chloride
Incat 6: Isotridecyloxypropylbis(3-hydroxypropyl)methylammonium chloride
Incat 7: Isotridecyloxypropylbis(dihydroxypropyl)methylammonium chloride
Incat 8: N-(branched) C_{16} alkyloxypropylbis(2-hydroxyethyl)methylammonium chloride
Incat 9: Tallowoxypropylbis(2-hydroxyethyl)methylammonium chloride
Incat 10: C_{10-12} alkyldioxypropylbis(3-hydroxypropyl)methylammonium chloride
Incat 11: C_{10-12} alkyldioxypropylbis(poly(5)hydroxypropyl)methylammonium chloride
Incat 12: C_{10-12} alkyldioxypropyltrimethylammonium chloride

Quaternary Ammonium Cationic Surfactants Not Within the Scope of the Invention

Noncat-1 N-isotridecyloxypropyl-N,N^1,N^1-tris(2-hydroxy ethyl)-N,N^1-dimethyl-1,3-propanediammonium dichloride
Noncat-2 Cocotrimethylammonium methylsulfate
Noncat-3 Ditallowdimethylammonium chloride
Noncat-4 Tallowbis(2-hydroxyethyl)methylammonium chloride
Noncat-5 Distearyldimethylammonium chloride
Noncat-6 (Branched) C_{18} alkyltrimethylammonium chloride
Noncat-7 Isotridecyloxypropylbis(2-hydroxyethyl) amine
Noncat-8 Benzethonium chloride monohydrate

Anionic Surfactants

LAS Sodium dodecyl benzene sulfonate
SLES Sodium C_{12-15} alkyl ethoxysulfate

Example I			
Oily Soil Removal			
	Control	Invention	Comparative
Formulation	1-0	1-1	1-2
Ingredient			
Basic Formulation	86.15	86.15	86.15
DASC-4 Whitener	0.30	0.30	--
NTS-1 Whitener	0.05	0.05	0.10
DASC-2 Whitener	--	--	0.45
Pareth 25-7	11.50	11.50	11.05
Pareth 25-3	--	--	1.70
Incat-1	--	2.96	--
Noncat-2	--	--	1.47
LAS	--	--	1.00
Washing Conditions : 37.7° C; 12 grains/gallon hardness			
Cloth Type	Reflectance Difference - RD Value		
TFI	9.5	14.1	10.9
Redep	0.4	0.5	0.7
Spangler	21.3	23.8	22.2
Redep	-0.3	-0.2	-0.1
DMO	12.6	13.6	11.6
Redep	-2.6	-1.0	-2.1
Total Change In Redeposition Cloth Whiteness	29.46	30.38	39.17

As can be seen from the reflectance data, for the TFI, Spangler and DMO soil-cloth tests, detergent compositions embodying the invention, on balance, provide better detergency results than are provided by the use of noninvention cationic surfactants. The sum of all whiteness differences for redeposition cloth tests, which are an indication of the degree to which the action of the fluorescers and redeposition of soil may be affected by surfactant performance, indicate that the invention compositions can be expected to present no signif-icant soil redeposition problems and should not have an adverse effect upon fluorescer performance.

Example II							
Oily Soil Removal							
	Control	Invention					Comparative
Formulation	2-0	2-1	2-2	2-3	2-4	2-5	2-6
Ingredient							
Basic Formulation	86.15	86.15	86.15	86.15	86.15	86.15	86.15
DASC-4	0.30	0.30	0.30	0.30	0.30	--	--
NTS-1	0.05	0.05	0.05	0.05	0.05	0.10	0.10
DASC-2						0.45	0.45
Pareth 25-7	11.50	11.50	11.50	11.50	--	11.05	11.05
Pareth 25-3						1.70	1.70
712					11.50		
Incat 1		1.47			1.47	1.47	
Incat 2			1.47				
Incat 3				1.47			
Noncat 2							1.47
LAS						1.00	1.00
Washing Conditions : 37.7½C; 12 grains/gallon hardness							
TFI	12.4	15.2	14.7	13.7	19.1	16.2	15.2
Redep	0.0	-0.2	-0.3	-0.5	-1.6	0.2	1.1
Spangler	21.6	22.5	22.2	21.9	20.9	23.1	22.4
Redep	-0.5	-0.5	-0.4	-0.6	-0.7	-0.5	-0.2
BBC	85.1	85.9	86.0	86.3	84.3	85.9	86.4
Redep	-2.7	-1.7	-1.8	-2.1	-2.9	-1.5	-1.5
DMO	11.4	11.6	11.0	11.0	12.5	11.9	10.9
Redep	-2.8	-1.4	-0.8	-0.5	-3.8	-1.2	-1.9
Total Change In Redeposition Cloth Whiteness	34.55	44.84	48.13	51.81	28.01	63.41	62.87

The data show that detergent compositions made in accordance with the invention are highly effective detergents for removing oily soils better than nonionic surfactants alone. They also exhibit minimal soil redeposition or loss of fluorescer activity even when compared to formulas containing no cationic surfactant. The comparison of the noninvention 2-6 with the invention 2-5 formula shows improved performance from the invention formulation even with the addition of LAS anionic to both formulas. The addition of LAS to the invention formulas is not necessary, while it is with formula 2-6.

Example III						
Oily Soil Removal						
	Control	Invention			Comparative	
Formulation	3-0	3-1	3-2	3-3	3-4	3-5
Ingredient						
Basic Formulation	86.15	86.15	86.15	86.15	86.15	86.15
DASC-4	0.30			0.7		
NTS-1	0.05	0.10	0.10	0.1	0.10	0.10
DASC-2		0.45	0.45		0.45	0.45
Pareth 25-7	11.50	11.05	11.05	11.05	11.05	11.05
Pareth 25-3		1.70	1.70	1.70	1.70	1.70
712						
Incat-1		1.47	1.47	1.47		
Noncat-2					1.47	1.47
LAS		1.00			1.00	
Washing Conditions : 37.7° C; 12 grains/gallon hardness						
TFI	14.4	18.3	17.4	17.8	16.9	18.1
Redep	1.8	2.7	2.9	2.4	2.5	2.6
Spangler	21.2	23.8	22.7	22.8	22.4	22.6
Redep	-0.6	0.2	-0.1	-0.4	0.1	-0.7
DMO	12.0	13.2	12.4	14.7	11.5	12.0
Redep	-2.4	-1.6	-1.2	-1.1	-1.7	-1.6
BBC	84.5	86.2	86.1	85.9	86.2	86.3
Redep	-2.4	-1.0	-1.1	-1.1	-1.2	-1.2
Total Change In Redeposition Cloth Whiteness	43.38	67.64	65.67	65.90	65.14	56.12

The data demonstrate that the invention detergent compositions are highly effective in removing a variety of stains from clothing with minimal soil redeposition and loss of brightener activity. Unlike the comparative formulas 3-4 and 3-5, anionic surfactants are not required with the invention formulas to give optimum brightening. When brightening is optimized with the comparative formulas, some detergency is lost. Comparisons of invention detergent formulations show little detergency or brightening differences with the addition of anionic surfactants. Thus, the invention formulations do not require addition of anionic surfactants for optimization of both detergency and brightening.

Example IV								
Evaluation of Brightener/Cationic Interaction								
	Control	Invention		Comparative				
Formulation	4-0	4-1	4-2	4-3	4-4	4-5	4-6	4-7
Basic Formulation	86.15	86.15	86.15	86.15	86.15	86.15	86.15	86.15
NTS-1	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
DASC-2	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Pareth 25-7	11.05	11.05	11.05	11.05	11.05	11.05	11.05	11.05
Pareth 25-3	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70
Incat-1		1.47	1.47					
Noncat-2					1.47	1.47		
Noncat-3				1.47				
Noncat-4							1.47	
Noncat-5								2.10
LAS		1.00			1.00			
Washing Conditions : 21.1 ° C; 9 grains/gallon hardness at 70 °, 100 ° and 130 ° F								
Total Change In Whiteness After								
1st Cycle	224.37	213.40	200.01	144.58	201.01	168.56	167.77	73.86
3rd Cycle	322.16	318.02	286.97	172.80	288.73	233.45	210.69	113.55
5th Cycle	355.02	350.51	312.64	179.03	320.68	258.54	220.79	131.24

The data demonstrates the effectiveness of the invention detergent compositions at whitening a composite of mixed fabrics through successive laundry cycles. Invention detergent 4-2 brightens fabrics better than any of the other cationic/nonionic comparative formulas. Only when anionic surfactant is employed to quench the comparative cationic does brightening equal the invention.

Example V

Oily Soil Remover Boosters

	Control	Invention			Comparative
Formulation	5-0	5-1	5-2	5-3	5-4
Ingredient					
Basic Formulation	86.15	86.15	86.15	86.15	86.15
DASC-4	0.30	--	--	--	--
NTS-1	0.05	0.10	0.10	0.10	0.10
DASC-2	--	0.45	0.45	0.45	0.45
Pareth 25-7	11.50	11.05	11.05	11.05	11.05
Pareth 25-3	--	1.70	1.70	1.70	1.70
AO					1.47
Incat 1		1.47			
Incat 4			1.47		
Incat 5				1.47	
Washing Conditions : 21.1°C; 3 grains/gallon hardness					
TFI	18.4	20.3	19.8	22.5	21.7
Redep	0.0	0.3	-0.3	0.3	0.3
Spangler	35.6	36.5	35.2	36.6	36.3
Redep	-0.4	-0.3	-0.6	-0.2	-1.2
DMO	12.7	10.3	11.8	12.1	12.3
Redep	-0.2	-0.8	-1.9	-1.4	-0.3
Washing Conditions : 21.1°C; 12 grains/gallon hardness					
TFI	9.4	13.1	10.3	13.0	11 3
Redep	-0.5	-0.5	-0.3	0.1	0.2
Spangler	22.6	22.3	22.0	23.6	22.9
Redep	-0.7	-0.5	-1.1	-0.3	-0.4

DMO	8.9	8.4	9.4	8.4	8.6
Redep	-1.3	-1.0	-1.9	-1.3	-1.2
Washing Conditions : 37.7°C; 3 grains/gallon hardness					
TFI	24.5	27.7	25.2	27.4	27.3
Redep	0.2	0.1	0.0	0.5	0.4
Spangler	33.2	35.6	35.3	36.2	35.5
Redep	-2.3	-1.1	-1.8	-1.0	-1.4
DMO	15.9	14.2	15.7	14.7	17.1
Redep	-0.7	-0.5	-2.1	-0.9	-0.3
Washing Conditions : 37.7°C; 12 grains/gallon hardness					
TFI	12.1	18.0	14.2	16.6	14.5
Redep	-0.8	-0.5	-0.3	-0.4	-0.6
Spangler	19.6	22.7	20.2	22.6	22.3
Redep	-2.1	-0.9	-1.1	-1.2	-1.4
DMO	12.7	13.9	12.5	12.8	12.2
Redep	-1.1	-0.1	-1.7	-0.9	-1.2
Washing Conditions : 54.4°C; 3 grains/gallon hardness					
TFI	26.0	30.0	28.3	30.1	26.8
Redep	0.4	0.0	0.4	-0.3	0.0
Spangler	32.8	34.6	33.1	34.3	33.1
Redep	-4.3	-3.4	-4.7	-3.0	-4.6
DMO	21.1	21.2	22.9	22.9	22.1
Redep	-1.0	-1.3	-1.6	-1.1	-0.7
Washing Conditions : 54.4°C; 12 grains/gallon hardness					
TFI	14.9	22.6	18.6	21.0	17.1
Redep	-0.6	-0.4	-0.4	-0.6	-0.2
Spangler	18.0	21.4	20.4	23.5	21.2
Redep	-8.4	-3.9	-4.2	-2.4	-5.9
DMO	15.6	19.4	15.8	19.0	16.7
Redep	-1.4	-0.8	-2.6	-1.3	-2.9
Total Change In Redeposition Cloth Whiteness	214.70	282.45	253.06	271.23	294.16

The data show the use of other ether amine-based quaternary ammonium cationic surfactants and their effectiveness over a wide range of temperatures and hardness. The amine oxide AO-17-2 is a type of nonionic surfactant and thus causes no brightener interference. However, detergency is not as great as with the cationic-containing invention formulas.

Example VI							
Oily Soil Removal, Various Cationics							
	Control	Invention				Comparative	
Formulation	6-0	6-1	6-2	6-3	6-4	6-5	6-6
Ingredient							
Basic Formulation	86.15	86.15	86.15	86.15	86.15	86.15	86.15
DASC-4	0.30	--	--	--	--	--	--
NTS-1	0.05	0.10	0.10	0.10	0.10	0.10	0.10
DASC-2	--	0.45	0.45	0.45	0.45	0.45	0.45
Pareth 25-7	11.5	11.05	11.05	11.05	11.05	11.05	11.05
Pareth 25-3	--	1.70	1.70	1.70	1.70	1.70	1.70
Incat-1		1.47					
Incat-6			1.47				
Noncat-1							1.47
Incat-8				1.47			
Incat-9					1.47		
Noncat-6						1.47	
Washing Conditions : 37.7° C; 12 grain/gallon hardness							
TFI	13.2	18.4	20.7	20.1	17.3	18.9	17.3
Redep	0.6	0.8	0.6	0.6	0.6	0.7	0.3
EMPA	12.5	13.0	13.6	13.1	16.1	12.3	11.0
Redep	-1.4	-0.7	-1.1	-0.3	-1.1	-0.6	-1.5
Spangler	21.0	21.7	23.3	22.6	22.0	21.1	20.3
Redep	-1.3	-1.4	-0.3	-0.8	-1.0	-1.0	-0.9
DMO	12.3	12.5	14.0	12.3	12.3	12.5	11.3
Redep	-3.0	-1.3	-1.1	-2.1	-2.2	-2.0	-2.4
Total Change In Redeposition Cloth Whiteness	48.16	66.17	66.37	62.21	58.68	51.25	56.62

The data show that the invention detergents are effective laundering materials with minimal soil redeposition and no significant interfence with fluorescer activity. The performance of formula 6-5 indicates that carbon chain branching alone is not the key to detergency and whitener advantages.

Example VII								
Oily Soil Remover Employing Nonionic, Anionic and Cationic Systems								
Formulation	7-0	7-1	7-2	7-3	7-4	7-5	7-6	7-7
Basic Formulation*	83.65	83.65	83.65	83.65	83.65	83.65	83.65	83.65
DASC-4	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
NTS-1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Pareth 25-7	10.00	10.00	10.00	10.00	10.00	10.00		
712							10.00	10.00
Sodium Polyacrylate	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Incat-1	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
SLES		2.00						2.00
Sodium Lauryl Sarcosinate			2.00					
LAS				2.00				
Sodium Stearate					1.65			
Sodium C_{14-16} Olefin Sulfonate						1.00		
Washing Conditions : 37.7° C; 12 grain/gallon hardness								
TFI	17.7	15.6	16.3	15.4	17.0	17.2	20.7	17.5
Redep	1.0	1.0	0.8	0.9	0.9	1.0	-0.7	0.7
Spangler	20.9	23.4	21.6	22.7	22.6	23.1	21.6	22.3

The Basic Formulation used in Example VII is the same as in Example I, except amount of sodium tripolyphosphate is 45.00 PBW.

Redep	-0.4	-0.4	-0.7	-0.3	-0.8	-0.8	-1.4	-0.1
EMPA	14.2	11.9	13.4	11.3	12.0	11.8	10.6	11.0
Redep	-0.2	-0.6	-0.1	-0.8	-0.3	-0.1	-6.3	-0.7
DMO	19.2	15.7	17.7	16.5	16.2	16.4	14.0	13.5
Redep	-0.8	-2.0	-0.9	-1.7	-1.1	-1.3	-4.5	-0.8
Total Change In Redeposition Cloth Whiteness	46.31	49.15	46.05	51.55	45.88	46.98	26.59	67.19

The data demonstrates that when anionic surfactants are added to the invention formulations, detergency is reduced on oily soils. Thus, the invention is best employed without anionics being used. Formula 7-6 demonstrated severe oily soil redeposition which interfered with whiteness index results.

Example VIII

Oily Soil Removal, Comparison of Different Cationics

	Control	Invention					Comparative	
Formulation	8-0	8-1	8-2	8-3	8-4	8-5	8-6	8-7
Ingredient								
Basic Formulation	86.15	86.15	86.15	86.15	86.15	86.15	86.15	86.15
DASC-4	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
NTS-1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Pareth 25-7	11.50	11.05	11.05	11.05	11.05	11.05	11.05	11.05
Pareth 25-3	--	1.70	1.70	1.70	1.70	1.70	1.70	1.70

Incat-1	--	1.47	--	--	--	--	--	--
Incat-7	--	--	1.47	--	--	--	--	--
Noncat-7	--	--	--	--	--	--	--	1.47
Incat-10	--	--	--	1.47	--	--	--	--
Incat-11	--	--	--	--	1.47	--	--	--
Incat-12	--	--	--	--	--	1.47	--	--
Noncat-8	--	--	--	--	--	--	1.47	--
Washing Conditions : 37.7°C; 9 grain hardness								
TFI	18.4	23.7	23.7	21.0	22.6	23.5	22.2	20.7
Redep	0.0	0.2	0.3	0.0	0.3	0.5	0.3	-0.1
EMPA	14.6	18.4	19.8	22.3	18.0	19.1	12.5	16.7
Redep	-2.5	-1.6	-1.5	-1.6	-1.8	-2.3	-2.4	-1.3
Spangler	29.5	30.5	28.9	30.0	30.1	28.5	27.8	31.1
Redep	-2.8	-1.2	-1.4	-1.4	-1.8	-1.4	-1.2	-1.5
Grass	21.5	20.8	20.9	18.8	20.2	21.3	20.2	20.3
Redep	-1.1	-1.4	-1.3	-1.0	-1.1	-1.2	-1.8	-0.8
HCO	10.2	7.3	8.3	7.5	9.1	8.7	7.6	7.8
Redep	-18.6	-9.4	-14.3	-14.5	-16.0	-15.3	-10.8	-14.2
DMO	10.7	10.6	11.6	11.0	10.3	10.5	9.6	11.2
Redep	-5.0	-1.2	-1.5	-1.9	-2.8	-1.6	-1.1	-3.3
Total Change In Redeposition Cloth Whiteness	40.70	67.24	61.26	63.86	58.76	58.98	47.73	67.83

The data demonstrate the effectiveness of the invention detergents for laundering soiled fabrics on a variety of stains and soils with minimal brightener interference.

Example IX

Bandy Black Clay Soil Removal

The formulations 8-0 through 8-7, inclusive, were also employed to evaluate their effectiveness in cleaning Bandy Black Clay soil-stained fabrics. The washing conditions were: 37-7½C; 9 grains/gallon hardness. The results are reported in Table 9-1.

Table 9-1

Formulation	8-0	8-1	8-2	8-3	8-4	8-5	8-6	8-7
Bandy Black Clay	85.8	85.5	86.2	86.9	87.0	86.3	86.1	85.7
Redep	-1.4	-0.9	-1.2	-1.0	-1.2	-1.0	-1.0	-1.1
Total Values								
Whiteness	85.67	88.68	90.57	93.73	93.93	90.79	88.04	88.37
Whiteness RDP	11.45	15.78	15.17	16.08	15.11	15.03	13.12	13.98

The data demonstrate the effectiveness of the invention compositions for laundering soiled fabrics, retaining fluorescer effectiveness and avoiding soil redeposition.

Claims

1. A granular laundry detergent comprising at least one nonionic surfactant, at least one anionic flulorescent whitening agent or brightening agent, at least one builder and at least one cationic surfactant, characterised in that the cationic surfactant comprises a quaternary ammonium compound in which three of the substituents are lower alkyl or modified lower alkyl groups and the fourth substituent comprises a long chain alkyl or modified alkyl group joined to the nitrogen atom through an electronegative group.

2. A granular laundry detergent according to claim 1 wherein said nonionic surfactant is present in the range from 7 to 25% by weight, said fluorescer is present in the range from 0.05 to 1.5%, said builder is present in the range from 10 to 75 weight percent and said cationic surfactant is present in the range from 1 to 6 weight percent.

3. A granular laundry detergent according to claim 1 or claim 2 wherein said cationic surfactant has the general formula $R_1E_zR_2R_3R_4N^+X$; wherein R_1 is an alkyl group having from 8 to 24 carbon atoms; R_2, R_3 and R_4 are the same or different and each independently is an alkyl group having from 1 to 4 carbon atoms or a hydroxy alkyl radical having the formula $H(OR_5)_x$, wherein R_5 is an alkylene radical having from 1 to 4 carbon atoms and x is an integer in the range from 1 to 4; E is a divalent electronegative group and z is an integer in the range from 1 to 4; with a proviso that at least one of R_2, R_3 or R_4 must be an alkyl group having from 1 to 4 carbon atoms.

4. A granular laundry detergent according to claim 3 wherein said electronegative group has the formula $-A(CH_2)_c$ wherein A is selected from the group consisting of -COO-, -OCO-, -O-O, -OCOO-, -CONH-, -NHCO-, -OCONH- and -NHCOO-.

5. A granular laundry detergent according to claim 3 wherein said electronegative group is $-OCH_2CH_2CH_2-$.

6. A granular laundry detergent according to claim 3 or claim 4 or claim 5 wherein R_1 and R_2 each independently have the formula $H(OR_5)_x-$ and R_4 is methyl.

7. A granular laundry detergent according to any of claims 3 to 6 wherein R_2 and R_3 are each $HOCH_2CH_2-$.