

PATENT SPECIFICATION

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NO DRAWINGS

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(54) DETERGENT COMPOSITIONS

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to detergent compositions.

According to the invention a spray dried detergent composition is free (as hereinafter defined) of water-soluble phosphate and comprises alkylbenzene sulphonate detergent with or without synthetic anionic sulphonate and/or sulphate detergent, soap, nonionic detergent and water-soluble nitrilotriacetate, in a weight ratio of soap to total sulphonate and sulphate detergent in the range 1:10 to 1:2; a weight ratio of nonionic detergent to total sulphonate and sulphate detergent in the range 1:10 to 1:3 and a weight ratio of nitrilotriacetate to total sulphonate and sulphate detergent in the range 5:1 to 1:1.

Such a detergent composition provides excellent deterative properties and a desirable low level of foam, making it particularly suitable for use in automatic washing machines. Despite the relatively low hydration capacity of the sodium nitrilotriacetate (as compared to that of sodium tripolyphosphate, a builder salt conventionally employed in spray dried detergent compositions) the detergent composition has surprisingly good flow characteristics even when it contains a relatively large amount of moisture.

The alkylbenzene sulphonate may contain 10—18 carbons in the alkyl group (such as dodecyl or tridecyl benzenesulphonate). Preferably the alkylbenzene sulphonate is linear and has a high content of 3-(or higher) phenyl

isomers and a correspondingly low content (well below 50%) of 2-(or lower) phenyl isomers. In other words, the benzene ring is preferably attached in large part at the 3 or higher (e.g. 4, 5, 6 or 7) position of the alkyl group and the content of isomers in which the benzene ring is attached at the 2 or 1 position is correspondingly low. Particularly preferred materials are set forth in British Patent Specification No. 1,087,337. In these preferred materials, the average molecular weight of the alkylated benzene content is in the range 250 to 270, the alkyl groups are linear and contain a minimum of 85% of alkyl chains of 12 to 14 carbons with at least 10% having 12 carbons and at least 10% having 13 carbons and at least 10% having 14 carbons, and the alkylbenzene sulphonate comprises a minimum of 37% of 5-phenyl and higher isomers and a maximum of 27% of 2-phenyl isomers. A particularly preferred material has less than 20% (e.g. 18%) of 2-phenyl isomers and over 40% (e.g. 43%) of 5- and 6-phenyl isomers and a molecular weight (of the alkylated benzene content) about 262.

The preferred linear alkylbenzene sulphonate detergent, where present, may be employed in admixture (e.g. in weight proportions of 1:1, 1:2, or 2:1) with other anionic synthetic sulphonate and/or sulphate detergents. Among the preferred materials for this purpose are long chain olefin sulphonate detergents, particularly those containing long chain alkene sulphonates, long chain hydroxy-alkane sulphonates or mixtures of alkene-sulphonates and hydroxylalkanesulphonates. The olefin sulphonate detergents may be prepared, in known manner, by the reaction of sulphur trioxide with long chain olefins (of 8 to 25, preferably 12 to 21, carbon atoms) of the formula $RCH=CHR_1$, where R is alkyl and R_1 is alkyl or hydrogen, to produce a mixture of sultones and alkene-

5 sulphonic acids, which mixture is then treated to convert the sultones to sulphonates. Examples of other sulphate or sulphonate detergents are paraffin sulphonates, such as the reaction products of alpha olefins and bisulphites (e.g. sodium bisulphite) which are primary paraffin sulphonates of usually 10 to 20, preferably 15 to 20, carbon atoms; sulphates of higher alcohols; salts of α -sulphofatty esters (e.g. of 10 to 20 carbon atoms, such as methyl α -sulphomyristate or α -sulphotallowate).

10 Examples of sulphates of higher alcohols are sodium lauryl sulphate, sodium tallow alcohol sulphate, (which is another preferred material for use in admixture with the linear alkylbenzene sulphonate), Turkey Red Oil or other sulphated oils, or sulphates of mono- or di-glycerides of fatty acids (e.g. stearic mono-glyceride monosulphate), alkyl poly (ethenoxy) ether sulphates such as sulphates of condensation products of ethylene oxide and lauryl alcohol (usually having 1 to 5 ethenoxy groups per molecule); lauryl or other higher alkyl glyceryl ether sulphonates; poly (ethenoxy) ether sulphates such as sulphates of the condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule).

30 Examples of soaps are those of fatty acids such as lauric, myristic, stearic, oleic, elaidic, isostearic, palmitic, undecylenic, tridecylenic, pentadecylenic or other saturated or unsaturated fatty acids of 11 to 18 carbon atoms. Soaps of dicarboxylic acids may also be used, such as soaps of dimerized linoleic acid. Soaps of other higher molecular weight acids such as rosin or tall oil acids, e.g. abietic acid, may also be employed.

40 The synthetic anionic sulphonate on sulphate detergent and the soap are preferably sodium salts, but it is permissible to use salts containing, in whole or in part, other cations which are such as to impart water-solubility to the acidic portion of the molecule or to maintain its water-solubility, e.g. potassium, mixed sodium-potassium, triethanolammonium, diethanol ammonium or other alkanolammonium, magnesium (in cases where the magnesium salt is water-soluble), or ammonium.

50 The preferred ratio of the amount of soap to the total amount of the synthetic anionic sulphate and sulphonate detergent is in the range 1:6 to 1:4 on an anhydrous basis.

55 The non-ionic detergent may be composed of a hydrophobic portion (e.g. an aliphatic hydrocarbon moiety of 12 to 20 carbon atoms) and a polyethyleneoxide hydrophilic portion attached thereto. Particularly suitable types of nonionic detergents are those made by the addition of ethylene oxide to long chain alkanols to produce a product containing approximately 60% ethylene oxide units. Examples of these are a condensation product

of about 9 mols of ethylene oxide and one mol of a mixture of straight chain primary alcohols having 14, 16 and 18 carbon atoms (which mixture of alcohols may be produced by a well known process involving polymerization of ethylene with a Ziegler type catalyst); a condensation product of about 11 mols of ethylene oxide and one mol of a mixture of primary alcohols having 14 to 15 (or 16 to 20) carbon atoms, which alcohols have a minor proportion of ethyl or methyl branches and may be produced by the well known oxo process; and a condensation product of 10 to 11 mols of ethylene oxide and one mol of a mixture of secondary branched long chain alcohols, which condensation product is produced, in two stages, by first condensing one mol of the alkanol mixture with two mols of ethylene oxide, recovering the resulting intermediate adduct from the unreacted material, and then condensing that adduct with the remaining 8 to 9 mols of ethylene oxide. The cloud point of the preferred nonionic detergents (measured in a 1% solution in water) is generally in the range 80 to 90°C.

Other nonionic detergents include condensation products of alkyl phenols with ethylene oxide, e.g. the reaction product of isooctyl phenol with 6 to 30 ethylene oxide units; condensation products of alkyl thiophenols with 10 to 15 ethylene oxide units; ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol mono-oleate and manitan monopalmitate, and condensation products of polypropylene glycol with ethylene oxide.

105 The preferred weight ratio of the amount of nonionic detergent to total sulphate and sulphonate detergent is in the range 1:6 to 1:4.

The preferred nitrilotriacetate is the trisodium salt. It is, however, permissible to use other water-soluble salts, such as alkali metal (e.g. potassium or mixed sodium-potassium) or ammonium salts.

110 The preferred weight ratio of the amount of nitrilotriacetate to the total amount of synthetic anionic sulphate and sulphonate detergent is in the range 4:1 to 2:1.

As already indicated, the detergent compositions of this invention are essentially free of water-soluble phosphates such as orthophosphates and condensed phosphates (e.g. tripolyphosphates and pyrophosphates), the total content of water-soluble phosphate, if present at all, being at most 5% of the weight of nitrilotriacetate salt.

125 Other ingredients may be present, such as water-soluble silicates, which *inter alia* act as corrosion inhibitors. Sodium (or potassium) silicates, e.g. of $\text{Na}_2\text{O}:\text{SiO}_2$ mole ratio within the range 1:1 to 1:3.5, may be used. The amount of silicate may be, for example, up 130

to 100% of the weight of the synthetic anionic sulphate or sulphonate detergent, e.g. about 50% to 100% of the weight of the latter and about 5% to 10% of the total solids, depending on the amount and character of the other components.

Another suitable ingredient is sodium sulphate which acts, among other things, as a filler.

Various other materials may be added to the detergent mixture in suitable amounts. Materials such as higher fatty acid amides may be added to improve detergency and modify the foaming properties in a desirable manner. Examples are higher fatty alkanol-amides, preferably having 2 or 3 carbons in each alkanol group and a fatty acyl radical having 10 to 18, preferably 10 to 14, carbon atoms, such as lauric or myristic mono-ethanolamides, diethanolamides, and isopropanolamides. Tertiary higher alkyl amine oxides such as those having 10 to 18 carbons in one alkyl group, e.g. lauryl or myristyl dimethylamine oxide, may be added also. Fatty alcohols of 10 to 18 carbons such as lauryl or coconut fatty alcohols, or cetyl alcohol, are suitable additives also. A hydrotropic material such as a lower alkyl aryl sulphonate, e.g. sodium toluene or xylene sulphonate, can be added to assist processing. In general, these materials are added in minor amounts, usually from 0.5% to 10%, preferably 1% to 6%, based on the total solids.

The compositions may also contain optical brightening agents or fluorescent dyes (e.g. in amounts in the range 0.05% to 0.5%); germicides such as halogenated carbanilides, e.g. trichlorocarbanilide, halogenated salicylanilide, e.g. tribromosalicylanilide, halogenated bisphenols, e.g. hexachlorophene, halogenated trifluoromethyldiphenyl urea, and the zinc salt of 1 - hydroxy - 2 - pyridine-thione (e.g. in amounts in the range 0.02% to 2%); soil-suspending agents such as sodium carboxymethyl cellulose or polyvinyl alcohol, preferably both, or other soluble polymeric materials, such as methyl cellulose (the amount of suspending agent being, for example, in the range 0.05% to 2%); antioxidants such as 2,6 - di - tert - butylphenol, or other phenolic antioxidant materials (e.g. in amounts in the range 0.001% to 0.1%), colouring agents, bleaching agents and other additives.

Borax, e.g. in proportion of up to 10% (such as 1% to 5%) of the total solids may also be present.

In the case of spray dried products the spray drying may be effected by forcing an aqueous slurry of the ingredients through a spray nozzle at the top of a spray tower into which heated evaporative gas such as air or flue gas is introduced. The gas may be introduced at the top of the tower to flow co-

current with the sprayed material or into the lower part of the tower to flow counter-current. The composition is preferably dried to a total moisture content of 3% to 12%. The moisture content can be determined readily by a conventional Cenco (Registered Trade Mark) Moisture Tester (in which a predetermined weight of the dried composition on a balance pan is exposed to the heat of a hot electric lamp, situated at a predetermined distance from the sample, until the weight of the sample becomes constant, at which time the weight loss, due to evaporation of moisture, including water of hydration, is measured) or by conventional xylol distillation methods. The product is in the form of small hollow spheres which may be completely separated and about 0.006" to about 0.1" in diameter or may form aggregates of such spheres clumped together as unitary vesiculated structures having generally rounded smooth surfaces. The bulk density of the spray dried product may be, for example, in the range 0.3 to 0.4 g/cc. The particles may be treated with a suitable agent, (e.g. dusted with a small amount of colloidal silica) to improve their flowability, and may be packed in containers having walls of low moisture transmissivity.

The slurry to be sprayed may be formed in a crutcher (a mixing vessel equipped with a high speed stirrer) by adding the individual ingredients to water. Generally sodium nitrilotriacetate will be added in finely powdered form, preferably as the hydrate, to the sulphonate detergent mixed with water. Sodium sulphate is preferably added in its anhydrous form. The water content of the aqueous slurry is advantageously relatively low, e.g. in the range 25% to 35% or less, and the slurry need not be hot (e.g. it may be of 90°F). However, best dispersion of the soap in the slurry is attained by the use of higher temperatures (e.g. 160°F). For special purposes higher water contents (e.g. 45%) and high temperatures (e.g. 160°F) may be employed. The slurry is generally passed through a grinding device to ensure that it is a smooth, lump-free suspension of fine particles of solids such as sodium nitrilotriacetate and sodium sulphate before spraying. The temperature of the heated evaporative gas introduced into the tower may be relatively low (e.g. in the range 350 to 450°F) but higher temperatures (e.g. in the range 600 to 700°F) may be employed if desired. The temperature of the powder leaving the bottom of the spray tower may be relatively low, e.g. about 100°F, or it may be higher (e.g. 140°, 160° or 200°F) particularly when the incoming evaporative gas is at a high temperature.

The following Examples illustrate the invention. All parts and percentages therein and throughout the specification are by weight unless otherwise specified.

EXAMPLE 1

In a crutcher there were mixed 16 parts of water; 14 parts of an aqueous slurry containing 47.7% sodium linear tridecylbenzene sulphonate; 10.6 parts of aqueous sodium silicate of 43.5% concentration (in which the $\text{Na}_2\text{O}:\text{SiO}_2$ mol ratio was 1:2.35) 27.7 parts of anhydrous sodium sulphate; 1.3 parts of the ethoxylation product made from ethylene oxide and primary alkanols (made by the oxo process) of C_{11} — C_{13} chain length, the ethoxylation product containing 11 mols of oxyethylene per mol of alkanol; 0.3 part of sodium carboxymethylcellulose; 0.33 part of fluorescent brighteners; 0.13 part of polyvinyl alcohol; 0.1 part of ultramarine blue; 0.015 part Polar Brilliant Blue RAW (Registered Trade Mark) (Geigy); 0.02 part of a phenolic antioxidant (Iphol 033); 1.9 parts of hydrated sodium soap of a mixture of tallow fatty acids and coconut oil fatty acids (in 3:1 weight ratio of tallow acids; coconut acids); and 17.2 parts of trisodium nitrilotriacetate hydrate.

The material was kept in heated condition, at a temperature of about 160°F . during the mixing operation. It was then spray dried.

The spraying was carried out in a spray tower into which the hot slurry was sprayed into a counter-current stream of hot air. On entering the tower the hot air had a temperature of about 425°F and was at substantially atmospheric pressure, while the mixture being sprayed had a temperature of 160°F . The free-flowing spray-dried particles, having a moisture content of 9 to 10%, were hollow beads, which in some instances adhere together in small clumps; on leaving the tower their temperature was in the range 100 to 140°F .

The brighteners used in the above formulation comprised (a) a naphthotriazole stilbene sulphonate brightener (Geigy "Tinopal (Registered Trade Mark) RBS—200%"), (b) another stilbene brightener bis (anilino diethanolamino s-triazinyl) stilbene disulphonic acid (c) another stilbene brightener, sodium bis (anilino morpholino s-triazinyl) stilbene disulphonate, and (d) an oxazole brightener, having a 1-phenyl 2-benzoxazole ethylene structure. The proportions of these in Example 1 were (a) 0.053 part, (b) 0.053 part, (c) 0.158 part, and (d) 0.066 part.

The hydrated soap (whose moisture content was about 30%) was fed to the crutcher in molten condition.

The alkylbenzenesulphonate (of the type described in British Patent Specification No. 1,087,337) contained about 18% 2-phenyl isomers and about 43% 5- and 6-phenyl isomers; the molecular weight of its alkylbenzene content was 262.

EXAMPLE 2

Example 1 was repeated twice, omitting the Polar Brilliant Blue and reducing the amount of water to (a) 12 parts, and (b) 5 parts; similar results were obtained.

WHAT WE CLAIM IS:—

1. A spray dried detergent composition free (as herein before defined) of water-soluble phosphate and comprising alkylbenzene sulphonate detergent with or without other synthetic anionic sulphonate and/or sulphate detergent, soap, nonionic detergent and water-soluble nitrilotriacetate, in a weight ratio of soap to total sulphonate and sulphate detergent in the range 1:10 to 1:2, a weight ratio of nonionic detergent to total sulphonate and sulphate detergent in the range 1:10 to 1:3 and a weight ratio of nitrilotriacetate to total sulphonate and sulphate detergent in the range 5:1 to 1:1.

2. A detergent composition as claimed in Claim 1 in which the weight ratios of (a) soap, (b) nonionic detergent and (c) nitrilotriacetate to total sulphonate and sulphate detergent are in the ranges (a) 1:6 to 1:4 (b) 1:6 to 1:4 and (c) 4:1 to 2:1.

3. A composition as claimed in any of the preceding claims in which the nonionic detergent comprises an adduct of ethylene oxide and an alkanol of 12 to 20 carbon atoms, the content of ethylene oxide units of the nonionic detergent being approximately 60% and its cloud point being in the range 80 to 90°C .

4. A detergent composition as claimed in any of the preceding claims in which the alkylbenzene sulphonate detergent comprises one in which the average molecular weight of the alkylated benzene content is in the range 250 to 270, the alkyl groups are linear and contain a minimum of 85% of alkyl chains of 12 to 14 carbons with at least 10% having 12 carbons, at least 10% having 13 carbons and at least 10% having 14 carbons, and which comprises a minimum of 37% of 5-phenyl and higher isomers and a maximum of 27% of 2-phenyl isomers.

5. A detergent composition as claimed in any of the preceding claims in which the synthetic anionic sulphonate detergent content comprises sodium alkylbenzene sulphonate.

6. A detergent composition as claimed in any of the preceding claims which also contains sodium silicate and sodium sulphate.

7. A detergent composition as claimed in any of the preceding claims which is spray-dried into the form of a free flowing powder comprising hollow spheres.

EXAMPLE 1

In a crutcher there were mixed 16 parts of water; 14 parts of an aqueous slurry containing 47.7% sodium linear tridecylbenzene sulphate; 10.6 parts of aqueous sodium silicate of 43.5% concentration (in which the $\text{Na}_2\text{O}:\text{SiO}_2$ mol ratio was 1:2.35) 27.7 parts of anhydrous sodium sulphate; 1.3 parts of the ethoxylation product made from ethylene oxide and primary alkanols (made by the oxo process) of C_{14} — C_{15} chain length, the ethoxylation product containing 11 mols of oxyethylene per mol of alkanol; 0.3 part of sodium carboxymethylcellulose; 0.33 part of fluorescent brighteners; 0.13 part of polyvinyl alcohol; 0.1 part of ultramarine blue; 0.015 part Polar Brilliant Blue RAW (Registered Trade Mark) (Geigy); 0.02 part of a phenolic antioxidant (Iphol 033); 1.9 parts of hydrated sodium soap of a mixture of tallow fatty acids and coconut oil fatty acids (in 3:1 weight ratio of tallow acids; coconut acids); and 17.2 parts of trisodium nitrilotriacetate hydrate.

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The hydrated soap (whose moisture content was about 30%) was fed to the crutcher in molten condition.

The alkylbenzenesulphonate (of the type described in British Patent Specification No. 1,087,337) contained about 18% 2-phenyl isomers and about 43% 5- and 6-phenyl isomers; the molecular weight of its alkylbenzene content was 262.



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EXAMPLE 2

Example 1 was repeated twice, omitting the Polar Brilliant Blue and reducing the amount of water to (a) 12 parts, and (b) 5 parts; similar results were obtained.

WHAT WE CLAIM IS:—

1. A spray dried detergent composition free (as herein before defined) of water-soluble phosphate and comprising alkylbenzene sulphate detergent with or without other synthetic anionic sulphate and/or sulphate detergent, soap, nonionic detergent and water-soluble nitrilotriacetate, in a weight ratio of soap to total sulphate and sulphate detergent in the range 1:10 to 1:2, a weight ratio of nonionic detergent to total sulphate and sulphate detergent in the range 1:10 to 1:3 and a weight ratio of nitrilotriacetate to total sulphate and sulphate detergent in the range 5:1 to 1:1.

2. A detergent composition as claimed in Claim 1 in which the weight ratios of (a) soap, (b) nonionic detergent and (c) nitrilotriacetate to total sulphate and sulphate detergent are in the ranges (a) 1:6 to 1:4 (b) 1:6 to 1:4 and (c) 4:1 to 2:1.

3. A composition as claimed in any of the preceding claims in which the nonionic detergent comprises an adduct of ethylene oxide and an alkanol of 12 to 20 carbon atoms, the content of ethylene oxide units of the nonionic detergent being approximately 60% and its cloud point being in the range 80 to 90°C .

4. A detergent composition as claimed in any of the preceding claims in which the alkylbenzene sulphate detergent comprises one in which the average molecular weight of the alkylated benzene content is in the range 250 to 270, the alkyl groups are linear and contain a minimum of 85% of alkyl chains of 12 to 14 carbons with at least 10% having 12 carbons, at least 10% having 13 carbons and at least 10% having 14 carbons, and which comprises a minimum of 37% of 5-phenyl and higher isomers and a maximum of 27% of 2-phenyl isomers.

5. A detergent composition as claimed in any of the preceding claims in which the synthetic anionic sulphate detergent content comprises sodium alkylbenzene sulphate.

6. A detergent composition as claimed in any of the preceding claims which also contains sodium silicate and sodium sulphate.

7. A detergent composition as claimed in any of the preceding claims which is spray-dried into the form of a free flowing powder comprising hollow spheres.



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8. A detergent composition substantially as described in any of the Examples.

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