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DETERGENT COMPOSITIONS

William Gilbert Spangler, 14 Charles Place, Chatham, N.J. 07928, and Henry Daniel Cross III, Box 242A, Heyer's Mill Road, Colts Neck, N.J. 07722

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ABSTRACT OF THE DISCLOSURE

Built detergent composition for heavy duty washing of clothing in the presence of added hypochlorite. The composition contains an organic detergent, a builder salt, a small amount of sodium bromide or other alkali metal bromide, and preferably an enzyme material.

This application is a continuation-in-part application of copending application Ser. No. 642,729 filed June 1, 1967, now abandoned.

Heavy duty built detergents for use in washing clothes are well known in the art. Generally they contain an organic detergent and a substantial proportion of a builder salt, usually present in amount equal to or greater than the amount of organic detergent. It is common, especially in the washing of white or color fast garments or linen, for the housewife to add a hypochlorite bleach, usually sodium hypochlorite solution (i.e. conventional household chlorine bleach), to the wash water.

One aspect of this invention relates to novel heavy duty built detergent compositions which yield a much whiter and stain-free wash, when used in the presence of household chlorine bleach, than the known conventional commercial heavy duty built detergent compositions. The novel compositions of this invention contain an organic detergent, a builder salt and a small amount of alkali metal bromide. The amount of bromide (e.g. NaBr) is usually within the range of about ¼ to 1%, preferably about ¼ to ½%, of the total detergent composition. The lower proportions give a good bleaching and sanitizing effect without substantial undesirable residual odor on the washed clothes or damage thereto, when employed in conventional household washing machines at the usual concentration of about 0.15% in the wash water, together with about 90 p.p.m. of chlorine (supplied by ½ cup of the usual commercial aqueous 5¼% NaOCl solution). Thus the effects attained with the built detergent compositions of this invention, when using ½ cup of the commercial NaOCl solution, are superior to those attained with the best commercial built detergents in the presence of twice as much of the NaOCl solution.

Another aspect of this invention relates to novel heavy duty built detergent compositions which contain an enzyme which may be a protease or an amylase or a mixture thereof. Other builders include polycarboxylates such as polymaleic anhydride, vinyl-maleic anhydride interpolymers e.g. methyl vinyl ether-maleic anhydride, ethylene-maleic anhydride, etc.

The organic detergent is preferably of the anionically active type. Examples are water-soluble salts of higher molecular weight sulfoxy-containing detergents such as a sulfonate or sulfate having a long hydrophobic chain (of e.g. 10–20 carbon atoms). For example, there may be used a higher alkylbenzene sulfonate (preferably having 10–18 carbons in the alkyl group, such as dodecyl or tridecyl benzene sulfonate); a paraffin sulfonate; an olefin sulfonate (made, for example, by reacting highly diluted gaseous SO_3 with an alpha-olefin followed by heating with

alkali, and containing hydroxy alkanesulfonates and alkenyl sulfonates); or a fatty alcohol sulfate (e.g. a sulfate of a higher alkanol or a sulfate of an ethoxylated higher alkanol having 1–5, preefrably about 3, oxyethylene groups per molecule). Among the sulfated and sulfonated aliphatic compounds are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g., coconut oil monoglyceride monosulfate, tallow diglyceride monosulfate; the long chain pure or mixed alkyl sulfates, e.g., lauryl sulfate, cetyl sulfate; the hydroxy sulfonated higher fatty acid esters, e.g. higher fatty acid esters of low molecular weight alkylol sulfonic acids, e.g., fatty acid esters of isethionic acid; the fatty acid ethanolamide sulfates; the fatty acid amides of amino alkyl sulfonic acids, e.g., lauric amide of taurine, and the like. Other suitable synthetic anionic detergents include water-soluble soaps of higher fatty acids such as the sodium soap of a 75:25 mixture of tallow and coconut oil fatty acids.

Although the anionic detergents are preferred, cationic, non-ionic and amphoteric detergents may be also employed in whole or as part of the detergent component, provided they are compatible with the other elements of the composition under conditions of storage and use thereof. As cationic detergents there may be noted the long chain alkyl quaternary ammonium compounds, e.g., cetyl quaternary ammonium salts. Within this group are included cetyl tri-methyl ammonium chloride and cetyl pyridinium chloride. Another cationic agent is the diethylene amino ethyl oleyl amide product.

The non-ionic agents are also well known in the art including the polyoxyethylene ethers of alkyl aromatic hydroxy bodies (e.g., the alkylated polyoxyethylene phenols), the polyoxyethylene ethers of long chain aliphatic alcohols and the polyoxyethylene ethers of hydrophobic propylene oxide polymers, e.g., the condensate of ethylene oxide with polypropylene glycol which condensate contains 80% ethylene oxide and has a molecular weight of about 1700, and iso-octyl phenoxy polyoxyethylene ethanol having about 8.5 ethanoxy groups per molecule, and the like. Alkyl amine oxide detergents such as lauryl or myristal dimethyl amine oxides may be present.

Amphoteric detergents also are contemplated, examples thereof including the salts of higher alkyl beta amino propionic acids, e.g., sodium N-lauryl beta alanine; the higher alkyl substituted betaines such as lauryldimethylammonium acetic acid; and the imidazoline type exemplified by the disodium salt of 1-(2-hydroxyethyl)-1-(carboxymethyl) - 2 - (hendecyl) - 4,5 - dihydroimidazolinium hydroxide.

The anionic and cationic surface active agents are commonly used in the form of their water soluble salts. For the synthetic anionic compounds, the alkali metal (e.g. sodium, potassium) salts are preferred, though other salts such as ammonium, amine, alkylolamine, and alkaline earth metals (e.g. calcium, magnesium) salts may be used if desired. For the cationic agents the chloride, sulfate, acetate, and like salts may be employed satisfactorily.

When an alkyl benzene sulfonate detergent is used, its alkyl group may be essentially linear (and biodegradable) or branched chain (e.g. derived from propylene tetramer) and the alkyl-benzene sulfonate may be a blend containing various alkyl chain lengths. When linear alkyl groups are present, 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 (e.g. below about 50%). Particularly preferred materials are set forth in U.S. Patent 3,320,174, May 16, 1967, of J. Rubinfeld.

The builder salt is preferably a condensed phosphate alkaline salt such as polyphosphate or pyrophosphate, e.g. tetrasodium pyrophosphate, pentasodium tripolyphosphate (which may be present in either of its two common "Forms," or in a mixture of Forms, preferably Form II), sodium hexametaphosphate or the corresponding potassium salts, alone or in a mixture with each other. For solid compositions pentasodium tripolyphosphate is especially suitable; for liquid compositions, tetrapotassium pyrophosphate is particularly preferred. Other builders may be of a type well known in the art; although they may include alkali metal, alkaline earth metal, ammonium and various ethanolammonium salts, alone or in combination, the preferred builders are sodium and potassium salts. Examples are the water-soluble phosphates, silicates, carbonates, bicarbonates, borates, sulfates, and chlorides as well as salts of organic acids such as ethylene diamine tetraacetic acid or nitrilotriacetic acid. Combinations of a salt of nitrilotriacetic acid (e.g. the trisodum salt) with the condensed phosphate (e.g. in ratio about two parts of the former to three to six parts of the phosphate) are particularly effective.

The enzyme used may be a proteolytic enzyme which is active upon protein matter and catalyses digestion or degradation of such matter when present as in linen or fabric stain in a hydrolysis reaction. The enzymes may be effective at a pH range of say about 4–12, and may be effective even at moderately high temperatures so long as the temperature does not degrade them. Some proteolytic enzymes are effective at up to about 80° C. and higher. They are also effective at ambient temperature and lower to about 10° C. Particular examples of proteolytic enzymes which may be used in the instant invention include pepsin, trypsin, chymotrypsin, papain, bromelin, colleginase, keratinase, carboxylase, amino peptidase, elastase, subtilisia and aspergillopepidase A and B. Preferred enzymes are subtilisin enzymes manufactured and cultivated from spectial strains of spore forming bacteria, particularly *Bacillus subtilis.*

Proteolytic enzymes such as Alcalase, Maxatase, Protease AP, Protease ATP 40, Protease ATP 120, Protease L–252 and Protease L–423 are among those enzymes derived from strains of spore foaming bacillus, such *Bacillus subtilis.*

Different proteolytic enzymes have different degrees of effectiveness in aiding in the removal of stains from textiles and linen. Particularly preferred as stain removing enzymes are subtilisin enzymes.

Metalloproteases which contain divalent ions such as calcium, magnesium or zinc bound to their protein chains are of interest.

The production of various proteolytic enzyme concentrates is described in the patent literature: for example in German Offenlegenschrift 1,800,508 and in published Dutch patent application 6,815,944.

Instead of, or in addition to, the proteolytic enzyme, an amylase may be present such as a bacterial amylase of the alpha type (e.g. obtained by fermentation of *B. subtilis*). One very suitable enzyme mixture contains both a bacterial amylase of the alpha type and an alkaline protease, preferably in proportions to supply about 100,000 to 400,000 Novo alpha-amylase units per Anson unit of said alkaline protease.

The enzyme prepartion may be incorporated as a powdered salt-containing product, or as a product containing little or no salt. A suitable range for the enzyme material is .001 Anson unit to 10 Anson units and preferably .1 Anson unit to 2 Anson units per 100 grams of total detergent composition.

The detergent composition generally contains in the range of about 5 to 45% (on a solids basis) of organic synthetic detergent. The amount of builder salt is generally at least about equal to two-thirds the amount of organic detergent. Preferred solid detergent compositions contain about 10 to 20% of the organic detergent and,

usually, in the range of about two to eight (preferably about two to five) parts of builder salt per per of detergent. Preferably the proportion and character of the builder salt are such that a 0.15% solution of the built detergent composition in water has a pH of about 9½ to 11.

When the composition is to be used for washing of fabrics containing nylon which, as is well known, tend to become yellowed on aging, it is desirable to include bleach-stable brightening agents and coloring agents in the built detergent composition. Particularly suitable brightening agents of this type are the known triazole stilbene brightening agents, such as the naphthotriazole stilbene mono-, di- or poly-sulfonates having the sulfonate substitution vicinal to the ethylenic bridge or on any of the positions of the naphthalene ring. The amount of such brightener may be for instance about 0.05% to 0.1% or more.

Other ingredients which may be present in the detergent composition are ingredients to give an additional germicidal effect such as halogenated carbanilides, e.g. trichlorocarbanilide, halogenated salicylanilide, e.g. tribromosalicylanilide, halogenated bis-phenols, e.g. hexachlorophene, halogenated trifluoromethyldiphenyl urea, zinc salt of 1-hydroxy-2-pyridinethione and the like (e.g. in amount in the range of about 0.01 to 5%); soil-suspending agents such as sodium carboxymethyl cellulose or polyvinyl alcohol, or a combination of these two, or other suitable soluble polymeric materials (the amount of suspending agent being, for example, in the range of about 0.1 to 2%); other brighteners; foam boosters, e.g. mono- or diethanolamides of long chain fatty acids, such as the monoethanolamide of coconut oil fatty acids or of a 70:30 lauric-myristic acid blend (e.g. present in proportion of about ½ to 3%).

As previously indicated, the compositions of this invention are highly useful for use in the washing of clothes in the presence of sodium hypochlorite solution. In place of the latter, the other sources of hypochlorite chlorine (i.e. chlorine present in hypochlorous ion, OCl^-) may be added to the wash water. These may be, for instance, water-soluble dry solid materials which generate hypochlorite ion on contact with, or dissolution in water. Examples thereof are the dry, particulate heterocyclic N-chloro imides such as trichloroisocsyaniric acid, and dichloroisocyanuric acid and salts thereof such as sodium dichlorisocyranurate and potassium dichloroisocyanurate. Other imides may also be used as N-chlorosuccinimide, N-chloromalonimide, N-chlorophthalimide and N-chloronaphthalimide. Additional suitable imides are the hydantoins such as 1,3-dichloro 5,5 dimethyl hydantoin; N-monochloro - 5,5 - dimethylhydantoin; methylene-bis (N-chloro-5,5-dimethylhydantoin); 1,3-dichloro-5-methyl-t-n-amylhydantoin, and the like. Other useful hypochlorite-liberating agents are trichloromelamine, N,N-dichlorobenzoylene urea, N,N-dichloro-p-toluenesulfonamide and dry, particulate, water soluble anhydrous inorganic salts such as lithium hypochlorite and calcium hypochlorite.

The following examples are given to illustrate this invention further. In these examples and in the remainder of the application, all proportions are by weight unless otherwise indicated.

EXAMPLE 1

One suitable spray-dried detergent composition has the following approximate overall composition: 10% sodium linear tridecylbenzenesulfonate; 2% of the ethoxylation product made from ethylene oxide and primary alkanols of C14–C15 chain length, the ethoxylation product containing 11 moles of oxyethylene per mol of alkanol; 2% of sodium soap of a mixture of 3 parts of tallow fatty acids and 1 part of coconut oil fatty acids; 34% of sodium sulfate; 34% of phosphate solids; 7% of sodium silicate solids (Na_2O:SiO_2 mol ratio 1:2.35); 0.25% of sodium

bromide; 0.15% of ultramarine blue; 0.5% of sodium carboxymethyl cellulose; 0.2% of water-soluble polyvinyl alcohol; 0.44% of fluorescent brighteners; 1.5% of Phthalocyanine Blue WD; 0.01% of a phenolic antioxidant ("Iphol") and the balance moisture.

The composition is prepared by separately spray drying a light blue colored formulation and a dark blue formulation and mixing the resulting two spray dried powders in the proportions of 95:5 (light blue: dark blue), to give a detergent formulation having a speckled appearance.

The light blue powder is made by spraying an aqueous slurry containing the ingredients described above (without the Phthalocyanine Blue); the phosphate in the composition is supplied by the addition of anhydrous pentasodium tripolyphosphate to the hot 165° F.) aqueous mixture just before spraying the resulting slurry. The dark blue powder is made by spraying a mixture containing 96.7% of this slurry and 3.3% of an aqueous 30% dispersion of the Phthalocyanine Blue WD. The solids content of each slurry before spraying is about 60% (i.e. the slurry has a total moisture content of about 40%).

The spraying is carried out in a spray tower into which the hot slurry is sprayed into a counter current stream of hot air. On entering the tower the hot air has a temperature of about 700° F. and is at substantially atmospheric pressure, while the mixture being sprayed has a temperature of 165° F. The spray-dried particles are hollow beads, which may be adhered together in small clumps.

The detergent composition is a stable mixture which is highly effective for the bleaching and washing of clothes in an automatic washing machine at a concentration of 0.15% in wash water containing one half cup of commercial sodium hypochlorite (providing 90 p.p.m. available chlorine) at a temperature of 120° F.

EXAMPLE 1B

Example 1 is repeated except that spherical beads of an enzyme material as post added to and blended with the spray dried detergent. The amount of enzyme material is such as to provide about 1 Anson unit per 100 grams of total composition. The enzyme employed is an alcalase material prepared by mixing the enzyme at about 55° C. with a melt formed by heating a waxy, water-soluble nonionic material (melting 45–50° C.) to about 60°. The non-ionic is a 20–25 mol ethylene oxide adduct with one mole of a C_{16} to C_{18} straight chain primary alkanol. The melt of enzyme and non-ionic is sprayed to form particles passing through a 20 mesh (U.S. Standard sieve size) and returned on a 100 mesh screen.

EXAMPLE 1C

Example 1B is repeated except that the enzyme employed is described as C372 in German published application 1,800,508.

In employing the enzyme-containing compositions of the present invention with the hypochlorite in the washing of clothes it is preferred to delay the addition of the hypochlorite for several (2–5) minutes after adding the detergent compositions of this invention to the wash cycle.

EXAMPLE 2

Another suitable spray-dried detergent composition (having a greater bleach-promoting effect than the composition of Example 1) has the following approximate overall composition: 15 parts sodium linear tridecylbenzenesulfonate; 25½ parts sodium sulfate; 34 parts phosphate solids; 7 parts sodium silicate solids (Na_2O:SiO_2 mol ratio 1:2,35); 5 parts trisodium nitrilotriacetate; 0.5 part sodium bromide; 0.1 part ultramarine blue; 0.003 part green dye (D & C Green #8); 0.075 part Phthalocyanine Blue WD; 0.5 part sodium carboxymethyl cellulose; 0.2 part water-soluble polyvinyl alcohol; 0.5 part fluorescent brighteners; 0.01 part phenolic antioxidant ("Iphol"), and 10 parts moisture.

The composition is prepared by separately spray drying a green colored formulation and a dark blue formulation and mixing the resulting two spray dried powders in the proportions of 95:5 (green:dark blue), to give a detergent formulation having a speckled appearance.

The green powder is made by spraying a slurry of the ingredients described above (without the Phthalocyanine Blue); the phosphate in the composition is supplied by the addition of anhydrous pentasodium tripolyphosphate to the hot (165° F.) aqueous mixture just before spraying the resulting slurry. The dark blue powder is made by spraying a mixture containing 96.7% of this slurry and 3.3% of an aqueous 30% dispersion of the Phthalocyanine Blue WD. The solids content of each slurry before spraying is about 60%.

The spraying is carried out in the same manner as described in Example 1.

The detergent composition is a stable mixture which is highly effective for the bleaching and washing of clothes in an automatic washing machine at a concentration of 0.15% in wash water containing one half cup of commercial sodium hypochlorite (providing 90 p.p.m. available chlorine) at a temperature of 120° F.

In both Examples 1 and 2 the brighteners include (a) a naphthotriazole stilbene sulfonate brightener (Geigy "Tinopal RBS–200%"), (b) another stilbene brightener, bis anilino diethanolaminotriazinyl) stilbene disulfonic acid (c) another stilbene brightener, sodium bis (anilino morpholino triazinyl) stilbene disulfonate, and (d) an oxazole brightener, having a 1-phenyl 2-benzoxazole ethylene structure. The proportion of these in Example 1 are (a) 0.071%, (b) 0.071%, (c) 0.21% and (d) 0.088%. The proportions of these in Example 2 are about (a) 0.09%, (b) 0.05%, (c) 0.25% and (d) 0.09%.

EXAMPLE 3

Example 2 is repeated except that in place of two thirds of the alkylbenzenesulfonate there is used an olefin sulfonate of 15 to 18 carbon atoms (made by reaction of the corresponding alpha-olefin and highly diluted SO_3 followed by neutralization with aqueous sodium hydroxide and heat treatment, to produce a mixture of sodium alkenyl sulfonates and the corresponding sodium hydroxyalkanesulfonates).

EXAMPLE 4

A suitable heavy duty liquid formulation contains 8.75% sodium linear tridecylbenzene sulfonate; 10% sodium salt of sulfate of ethoxylation product made from 3 mols ethylene oxide and one mol primary C14–C15 alkanol; 8.2% potassium xylene sulfonate; 1% lauric-myristic diethanolamide; ¼% sodium carboxymethyl cellulose; ¼% polyvinyl alcohol; 0.6% hydrogenated castor oil; 0.16% bis(anilino diethanolamino triazinyl) stilbene disulfonate (brightener); 0.06% naphthotriazole stilbene sulfonate brightener (Geigy "Tinopal RBS 200%"); 15% tetrapotassium pyrophosphate; 1.8% Na_2SO_4; ¼% NaBr; balance water with small amount of perfume.

EXAMPLE 5

Example 1 is repeated except that the 34% phosphate is replaced with 10% sodium salt of polymaleic acid and 24% sodium sulfate.

EXAMPLE 6

Example 1 is again repeated replacing the phosphate with 10% sodium salt of a vinyl methyl ether-maleic anhydride interpolymer (1:1; specific viscosity=1.8).

While the preferred alkali metal bromide is the sodium bromide, it is within the broad scope of this invention to employ other alkali metal bromides (e.g. KBr or LiBr) in place of all or a part (e.g. ⅓) of the sodium bromide.

The compositions of this invention may be used for the washing of fabrics containing natural fibers such as cotton and linen, or blends of such fibers (e.g. durable press cotton-polyester blends). They may be used for washing