

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 89202650.1

(51) Int. Cl.⁵: **C11D 3/386 , C11D 3/37 , C11D 1/72**

(22) Date of filing: 20.10.89

(30) Priority: 21.10.88 US 261051

(43) Date of publication of application: 25.04.90 Bulletin 90/17

(54) Designated Contracting States: BE CH DE ES FR GB IT LI NL SE

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(54) **Heavy duty particulate synthetic organic nonionic detergent compositions of improved cleaning action on laundry containing hard-to-remove soils.**

(57) A heavy duty particulate synthetic organic nonionic detergent composition, which is preferably what may be termed concentrated or superconcentrated because of its highly effective combination of cleaning agents, so that relatively small proportions thereof may be utilized to effectively wash laundry and remove from it hard-to-remove soils that often are entrapped in the laundry fibers, and which tend to give laundry articles a grayish appearance, includes certain percentages of synthetic organic nonionic detergent, builder for such detergent, cellulase and other cleaning enzyme(s), especially protease, and water. Such detergent compositions preferably include protease and amylase with the cellulase, and the cellulase may be of a type derived from fungus. To further improve cleaning and soil removal they also include narrow range ethoxylate nonionic detergent and polyethylene terephthalate-polyoxy-ethylene terephthalate copolymer soil release promoting agent. In European-type detergent compositions, intended for use in European-type washing machines, which usually operate at higher temperatures, perborate bleaching agent is desirably present but American-type detergent compositions, which are often employed in lower temperature washing of laundry, usually omit such bleaching agent. The described compositions include phosphate and non-phosphate builder systems. Also within the invention are processes for washing laundry, preferably with the described compositions.

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HEAVY DUTY PARTICULATE SYNTHETIC ORGANIC NONIONIC DETERGENT COMPOSITIONS OF IMPROVED CLEANING ACTION ON LAUNDRY CONTAINING HARD-TO-REMOVE SOILS

This invention relates to laundry detergent compositions. More particularly, it relates to heavy duty particulate synthetic organic nonionic detergent compositions in which cellulase enzyme promotes removal of hard-to-remove soils, such as sebum/particulate soils from fibers of the fabrics of laundry being washed despite the facts that the concentration of the cellulase in the wash water is very low and that the concentration of detergent composition is less than normally employed. The particulate detergent composition is what may be termed a concentrated or super-concentrated composition and the charge thereof to a washing machine will be relatively small, often being less than two ounces per tub load of water, such as less than about 0.06% by weight. Within the invention are phosphate and non-phosphate detergent compositions, as well as bleaching and non-bleaching compositions.

Built nonionic detergent compositions of the Fresh Start® type have been described in the patent literature and have been successfully marketed. Such particulate detergents include a normally solid nonionic synthetic organic detergent that has been absorbed into the interiors of spray dried base beads of builder components, with some of the nonionic detergent coating the surfaces of the beads. Such compositions have been found to be benefited by the incorporation therein of soil release promoting agents such as polyethylene terephthalate-polyoxyethylene terephthalate (PET-POET) copolymers, which have been sold under the trade names Alkaril® QCF, Alkaril QCJ and Alkaril SRP-2-F (manufactured by Alkaril Chemical Company). Such materials are described in more detail in U.S. patents 4,569,772 and 4,571,303, of which the former discloses PET-POET copolymer stabilized with polyacrylate. In U.S. patent application S.N. 07/084,524 there are described detergent compositions of the Fresh Start type which are based on narrow range ethoxylate nonionic detergents (NRE's), which detergent compositions may include the PET-POET copolymer stabilized with polyacrylate. Enzymes of various types have long been employed in laundry products to aid in removing different types of soils from laundry, usually with the expectation that the enzyme would act to break down the soil and thereby promote its removal from the fibers of the laundry fabrics. Until recently the only really successful commercial applications of this principle were in some enzymatic laundry detergents containing protease and/or amylase, with the proteolytic enzymes being far more widely employed. However, enzymes had been incorporated in bleaches and pre-soaks. Cellulase had been suggested for detergent use in various patents and publications but until recently no successful commercial products have been marketed that included it. Among relevant patents that relate to employment of cellulase in detergent compositions are British specifications 1,368,599; 2,094,826; and 2,095,275; U.S. patents 4,435,307; 4,479,881; and 4,738,682; and European specifications 0,269,168; and 0,269,169. All the aforementioned patents and specifications are included herein by reference.

Although the patents and publications mentioned above which mention cellulase as an enzymatic component of a detergent composition for the greater part described compositions which were never marketed and never achieved any commercial success, applicants are aware of one cellulase-containing detergent composition which has been successfully marketed, which has been sold in Japan by Kao Soap Company, Ltd., under the tradename Attack. Such product is an anionic detergent which contains only a very minor proportion of nonionic detergent, and which utilizes cellulase obtained from bacteria, rather than cellulase obtained from fungi. The two enzymes are different in effect and presumably therefore they are also different in chemical structure, although the complexities of the structures have heretofore prevented scientists from obtaining knowledge as to the exact nature of such difference. Applicants have been informed and believe that before their work cellulase derived from fungus had been added to various detergent compositions, including Dynamo® and Fresh Start. However, the amounts employed were in substantial excess of the upper limits of the cellulase contents of the present detergent compositions and the additional expenses involved could have made such products unacceptable in the market place. Applicants have discovered that much smaller proportions of cellulase, especially fungus-derived cellulase, incorporated in their detergent compositions, preferably those based on NRE nonionic detergents, significantly aid in the removal, especially from cotton, of hard-to-remove, deep-down or embedded soils, according to test methods employed by applicants which are designed to simulate actual cleaning effects on hard-to-remove soils. Such effectiveness of the described composition is considered to be unexpectedly beneficial, especially in view of the employment of applicants' small proportions of cellulase and because similar concentrations of such cellulase in anionic detergent compositions and in wash waters containing such compositions do not improve removals of such soils.

In accordance with the present invention a heavy duty particulate synthetic organic nonionic detergent composition which has significantly improved cleaning action against hard to remove soils in laundry fibers

when such laundry is soiled with such types of soils, comprises 4 to 30% of synthetic organic nonionic detergent, 25 to 80% of builder for such nonionic detergent, 0.1 to 2% of protease, 0 to 2% of amylase, 0.2 to 1% of cellulase, and 1 to 15% of water. The invented compositions include both phosphate-built and non-phosphate products, bleaching and non-bleaching detergent compositions, and the invention also includes washing processes in which such compositions or components thereof are employed. Such compositions also preferably include NRE-type nonionic detergent, PET-POET copolymer and stilbene-type fluorescent brightener. Preferably the enzyme system will include protease, amylase and cellulase, in prilled forms, and it may also be preferable, in many instances, for the cellulase to be derived from fungus.

The active detergent constituents of the present compositions and methods is a nonionic detergent, or more accurately, a mixture of such detergents. Anionic synthetic organic detergent compositions are not improved in cleaning action against deeply embedded laundry soils by small proportions of fungus-derived cellulase, e.g., 0.5%, whereas in the present detergent compositions, based on nonionic detergents, such improvements have been obtained. However, small proportions of anionic detergents may be employed in essentially nonionic detergent compositions without having objectionably detrimental effects. Amphoteric detergents may be present with nonionic detergents in these compositions but cationic surfactants are usually omitted if any anionic detergent is present.

Of the nonionic detergents it is preferred to employ those which are reaction or condensation products of ethylene oxide and a suitable lipophile or lipophilic material. Higher alcohols, usually fatty alcohols of 10 or 12 to 18 carbon atoms per molecule, are the preferred reactants with ethylene oxide to make the desired nonionic detergents for the compositions of this invention but Oxo-type alcohols and C_7-10 alkyl substituted phenols, such as nonyl phenols, may also be useful. Other members of this well known class of nonionic detergents, such as higher fatty acid esters of ethylene oxide may also be useful in some compositions and for particular applications but preferably a higher fatty alcohol is employed as the source of the lipophile, and very preferably, for best cleaning results, the product is a narrow range ethoxylate nonionic detergent. By narrow range ethoxylate is meant a polyethoxylated lipophile, ethoxylated with ethylene oxide so that at least 70% of the ethylene oxide in the nonionic detergent is in polyethoxy groups having n to $(n+8)$ moles of ethylene oxide per mole, wherein n may be from 1 to 10, although it is preferable that n be 3 to 5, more preferably 4. Thus, such preferred narrow range ethoxylate (NRE) nonionic detergent has at least 70% of the ethylene oxide thereof in polyethoxy groups of 4 to 12 ethylene oxides. Most preferably, such groups are of 5 to 10 ethoxies and are at least 80 or 85% of the ethoxy content of the NRE's. Instead of ethylene oxide, in some cases mixtures of ethylene oxide and propylene oxide may be employed in such NRE's, providing that the final product has the desirable and beneficial cleaning properties, in combination with cellulase, as will be described in more detail later in this specification. Although it may be preferred for the polyethoxylates of the NRE's to be within certain ranges of ethoxy contents in the polyethoxy moieties thereof, manufacturing methods usually result in mixtures of polymers, so average ethoxy contents may be specified. Thus, the NRE nonionic detergents may be of an average of 4 to 12 or 5 to 10 ethylene oxide groups per mole, e.g., averaging about 6 or 7 EtO's per mole. The preferred lipophile will be that from higher fatty alcohol and therefore the ethylene oxide content of the NRE nonionic detergents will be at least 70% of higher fatty alcohol ethoxylates of 5 to 10 ethylene oxide groups per mole and more preferably, at least 80 or 85% of the ethylene oxide will be in such higher fatty alcohol ethoxylates. This compares with about 50% or less of such polyethoxy groups in BRE (the older and more common broad range ethoxylates). Also, the higher alcohol may be primary or secondary alcohol, but fatty alcohols are preferred. The higher alcohol ethoxylates will preferably be of 12 to 14 carbon atoms, although sometimes the alcohol may be of 10 to 16 or 12 to 16 carbon atoms. It is within the invention to employ synthetic lipophiles, such as those derivable from higher alcohols of odd numbers of carbon atoms in the ranges given, as well as those that can be obtained from alcohols of even numbers of carbon atoms, as in natural products, and mixtures thereof may also be utilized.

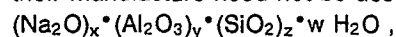
Among the preferred NRE nonionic detergents employable in accordance with the present invention is Tergitol® Nonionic Surfactant 24-L-60N, which is of the formula $RO(CH_2CH_2O)_nH$, wherein R is a mixture of C_{12} and C_{14} linear alcohols and n averages about 7.0. Such product has a cloud point of $60^\circ C$. for a 1% aqueous solution and is a narrow range ethoxylate. Its properties are described in a product information bulletin issued by the manufacturer, Union Carbide Corporation, which carries the date of April, 1987. In place of Tergitol Nonionic Surfactant 24-L-60N there may also be employed similar products manufactured by Shell Chemical Company, which have been identified as Shell® 23-7P and Shell 23-7Z.

Various builders and combinations thereof which are effective to complement the washing action of the nonionic synthetic organic detergent(s) and to improve such action include both water soluble and water insoluble builders. Of the water soluble builders, both inorganic and organic builders may be useful, but the inorganics are preferred, usually as alkali metal salt(s). Among the water soluble inorganic builders those of

preference include: various phosphates, usually polyphosphates, such as the tripolyphosphates and pyrophosphates, more specifically the sodium tripolyphosphates and sodium pyrophosphates, e.g., pentasodium tripolyphosphate, tetrasodium pyrophosphate; sodium carbonate; sodium bicarbonate; sodium silicate; sodium borate or borax; and mixtures thereof. Instead of a mixture of sodium carbonate and sodium bicarbonate, sodium sesquicarbonate will sometimes be substituted. The alkali metal or sodium silicate employed is normally of $M_2O:SiO_2$ or $Na_2O:SiO_2$ ratio within the range of 1:1.6 to 1:3, preferably 1:2.0 to 1:2.8, e.g., 1:2.4 (or 1:2.35).

Of the water soluble inorganic builder salts, when phosphates are not restricted by law or regulation they may be employed, often with a lesser proportion of sodium silicate. In preferred non-phosphate compositions carbonates may be employed with bicarbonates, often with a lesser proportion of sodium silicate, and with borates being optional. Silicates will rarely be used alone. Instead of individual polyphosphates being utilized it may sometimes be preferred to employ mixtures of sodium tripolyphosphate and sodium pyrophosphate in proportions within the range of 1:10 to 10:1, preferably 1:5 to 5:1. Of course, it is recognized that changes in phosphate chemical structure may occur during crutching and spray drying so that the final product may differ in phosphate content somewhat from the phosphate components charged to the crutcher, as they have been set forth in the present description. Similarly, bicarbonate decomposes to carbonate, often to a 1/3 to 1/2 extent, during spray drying but the percentages of such components given in this specification are for the final product compositions. Although sometimes water soluble organic builders may be employed too, such as sodium citrate, trisodium nitrilotriacetate (NTA), and polyacetal carboxylates (Builder U), the water soluble inorganic builders are generally preferred, as was previously indicated. An exception is sodium citrate, often used as the dihydrate, which helps to raise the bulk density of the final product, which is of advantage when a concentrated product is desired. The various water soluble builder salts may be utilized in hydrated forms, which are sometimes preferred, and the water soluble builders, hydrated or anhydrous, will normally be sodium salts, or mixtures of alkali metal salts, but sodium salts are usually preferred. In some instances, as when neutral or slightly acidic detergent compositions are being produced, acid forms of the builders may be preferable but normally the salts will either be neutral or basic in nature, and usually a 1% aqueous solution of the detergent composition will be of a pH in the range of 8 to 11.5, e.g., 8 or 9 to 10 or 10.5.

Insoluble builders, generally of the Zeolite A type, usually hydrated, as with 15 to 25% of water of hydration, may be used advantageously in the compositions of the present invention. Hydrated Zeolites X and Y may be useful too, as may be naturally occurring zeolites and zeolite-like materials and other ion-exchanging insoluble compounds that can act as detergent builders. Of the various Zeolite A products, Zeolite 4A may often be found to be preferred. Such materials are well known in the art and methods for their manufacture need not be described here. Usually such compounds will be of the formula



wherein x is 1, y is from 0.8 to 1.2, preferably about 1, z is from 1.5 to 3.5, preferably 2 to 3 or about 2, and w is from 0 to 9, preferably 2.5 to 6.

The zeolite builder should be a univalent cation exchanging zeolite, i.e., it should be an aluminosilicate of a univalent cation such as sodium, potassium, lithium (when practicable) or other alkali metal, or ammonium. Preferably the univalent cation of the zeolite type mentioned is an alkali metal cation, especially sodium or potassium, and most preferably it is sodium, as was indicated in the preceding formula. The zeolites, whether crystalline or amorphous, are capable of reacting sufficiently rapidly with calcium ions in hard water so that, alone or in conjunction with other water softening compounds in the detergent composition, they soften the wash water before adverse reactions of water hardness ions with other components of the synthetic organic detergent composition occur. The zeolites employed may be characterized as having a high exchange capacity for calcium ion, which is normally from about 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of the aluminosilicate, preferably 250 to 350 mg. eq./g., on an anhydrous zeolite basis. Also they preferably reduce the hardness quickly in wash water, usually within the first 30 seconds to five minutes after being added to the wash water, and they can lower the hardness to less than a milligram, as $CaCO_3$, per liter within such time. The hydrated zeolites will normally be of a moisture or water of hydration content in the range of 5 to 30%, preferably about 15 to 25% and more preferably 17 to 22%, e.g., about 20%. The zeolites, as charged to a crutcher mix from which base beads may be made, should be in finely divided state, with the ultimate particle diameters being up to 20 microns, e.g., 0.005 to 20 microns, preferably 0.01 to 8 microns mean particle size, e.g., 3 to 7 microns, if crystalline, and 0.01 to 0.1 micron, e.g., 0.01 to 0.05 micron, if amorphous. Although the ultimate particle sizes are much lower, usually the zeolite particles are of sizes within the range of No. 100 to 400 sieve, preferably No. 140 to 325 sieve, as charged to the crutcher for the manufacture of the base beads. While it is often preferred to employ spray dried base beads, which may

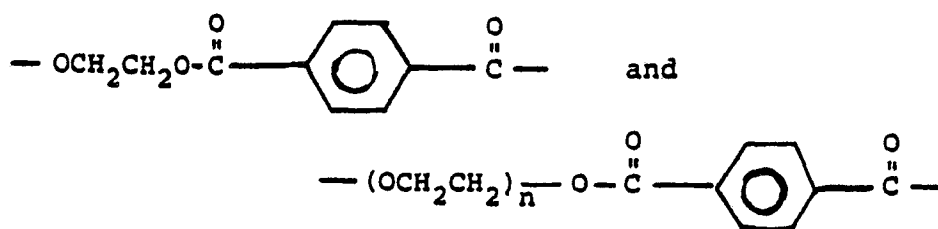
sometimes include a part of the detergent component and some adjuvants, it is also within the invention to make the present detergent composition by mixing the components thereof, most of which will be finely divided granular solids, but a minor proportion of which can be in liquid state at the time of mixing. In the parlance of the art, tower or non-tower manufacturing processes may be employed.

5 The cellulolytic enzyme, cellulase, which is employed in the present invention, is a fungal cellulase, which is producible by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*). Such material, its characteristics, its manufacture and its use in detergent compositions have been described in U.S. patent 4,435,307. Other cellulases are also useful in the practice of this invention but most of the applicants' work has been done with the described (and preferred) fungal cellulases, which produce the desired "deep"
10 cleaning of soiled laundry when such cellulases are incorporated into the described compositions. Additional cellulases are described in British patent specification 2,094,826, and such may be employed in the present invention, but the desired results are thought to be best obtained by utilizing the preferred cellulase. Such is obtainable from Novo Industri A/S under the trademark Celluzyme® 1500T, which has an activity of 1,500 CMC units/gram, but their 1,200 CMC units/gram SP-227 may also be employed.

15 With the cellulase there are preferably employed other enzymes which coact with the cellulase in the removal of hard to remove soils from laundry substrates. Such compatible materials include proteolytic, amylolytic and lipolytic enzymes, any or all of which may be employed with the cellulase. However, it appears that the proteolytic enzymes are most important in combination with cellulase, and mixed proteolytic/amylolytic enzymes, in combination, are even more preferred with the cellulase. In such
20 combinations of enzymes it appears that the proteolytic and amylolytic enzymes work to decompose the stain material, making it easier to remove, and the cellulase helps to make the substrate more "approachable" or attackable by the other enzymes, thereby aiding in removing hard to remove and deep down stains during washing operations. Among useful proteolytic enzymes are those identified by the trademark (Maxatase®, sold by Gist Brocades), while examples of amylolytic enzymes include Termamyl®
25 obtainable from Novo Industri A/S.

Among other components of the present compositions which coact with the cellulase and other components of applicants' compositions in helping to remove difficult stains from laundry items there may be mentioned the copolymers of polyethylene terephthalate and polyoxyethylene terephthalate (PET-POET copolymers), which are known to be effective as soil release promoters. Such materials are preferably
30 incorporated in the present detergent compositions together with polyacrylate stabilizers for them, and the polyacrylates contribute additional cleaning and suspending properties to the compositions. The PET-POET copolymers and the polyacrylates also coact with the NRE nonionic detergents to promote better cleaning of substrates.

The PET-POET copolymers employed will usually be of molecular weights in the range of 15,000 to
35 50,000, preferably 19,000 to 43,000, e.g., about 30,000 or 40,000, according to molecular weight determinations performed on samples of materials of such types, as described herein. Such molecular weights are weight average molecular weights. In the polymers utilized the polyoxyethylene will usually be of a molecular weight in the range of about 1,000 to 10,000 and the molar ratio of polyethylene terephthalates to polyoxyethylene terephthalate units (considering
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45 as such units) will be within the range of 2:1 to 6:1. The proportion of ethylene oxide to phthalic moiety in the polymer will normally be at least 10:1 and often will be 20:1 or more. Thus, it is seen that the polymer may be considered as being essentially a modified ethylene oxide polymer with the phthalic moiety being only a minor component thereof, whether calculated on a molar or weight basis.

50 The described PET-POET copolymer is obtained from Alkaryl Chemical Company as Alkaryl SRP-2-F, which also contains 5% of polyacrylate stabilizer. Although it is used by applicants in accordance with the present invention, and is highly preferred for its desired functions, other PET-POET polymers, such as those described in British Specification 1,088,984 and in U.S. patent 3,962,152 may also be employed and sometimes can be effective soil release promoting agents in the compositions and methods of this
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invention. However, the soil release promoting properties of such materials are usually not as good as those of the preferred polymers.

The polyacrylate used to stabilize the PET-POET copolymer may be a suitable water soluble polyacrylate, such as alkali metal polyacrylate, e.g., sodium polyacrylate, of molecular weight less 50,000, usually being within the range of about 1,000 to 5,000, preferably being in the range of 1,000 to 3,000 and most preferably being between 1,000 and 2,000, e.g., about 2,000. Although other water soluble polyacrylates may sometimes be substituted in part for the described sodium polyacrylate, including some other alkali metal polyacrylates, e.g., potassium polyacrylate, it is preferred that such substitutions, when permitted, be limited to a minor proportion of the material, and preferably the polyacrylate employed will be an unsubstituted sodium polyacrylate. Such materials are available from Alco Chemical Corporation, under the name Alcosperse®.

In addition to the stain removing components of the present invention, which cooperate with the cellulase and other enzymes in helping to remove embedded, deep-down or difficult-to-remove stains and soils from laundry substrates, other coacting components of preferred compositions of the invention are fluorescent brighteners. This well-known class of components include various heterocyclic materials, such as are described in British patent 2,094,826, but those which are preferred are the stilbene and distilbene fluorescent or optical brighteners, representative of which are the Tinopals, such as Tinopals® 5BM conc. and RBS, marketed by CIBA-Geigy, and Blancophors®. In the present compositions the fluorescent brighteners coact with the cellulase and other composition components, including the detergent, builder, other enzymes, soil release promoter, and oxygen or per-compound bleach, when present, to make such compositions produce whiter (and less dingy) laundry after repeated soilings and launderings. It appears that the cellulase acts on fibrous materials, especially cotton, to modify the fiber structures, and the fluorescent brightener may be better adsorbed by the substrate and therefore can be more effective in improving the white appearance of the laundry, counteracting "dingies" or any "tattletale-gray" appearance thereof.

In detergent compositions for the European market, wherein higher washing temperatures are employed, which can cause the release of active oxygen from oxygen bleaches, and thereby can promote bleaching of washed laundry without use of chlorine, oxygen bleaches may be desired components of the invented compositions. Among such the most preferred are the alkali metal perborates, especially sodium perborate monohydrate, although the tetrahydrate and other hydrates may also be used. To aid in the release of bleaching oxygen from the perborate, a perborate activator may be employed, such as any of those described in European specification 0,269,169, including tetraacetyl ethylenediamine (TAED), acyloxy benzene sulfonate, tetraacetyl hexamethylenediamine and tetraacetyl methylenediamine.

Various other adjuvants may be employed in the present compositions, including but not limited to: bleach stabilizing agents; suds controlling agents, e.g., sodium higher fatty acid soap; antioxidants; buffers, e.g., sodium propionate; soil suspending agents, e.g., sodium carboxymethyl cellulose, polyvinyl alcohol, polyvinyl acetates; dyes; perfumes; enzyme activators, such as cellulase activators, as described in British specification 2,094,826; filler salts, e.g., sodium sulfate; caking inhibitors, such as p-toluene sulfonic acid salts; flow promoters, e.g., magnesium silicate; solubilizers, such as urea; fabric softening agents, such as quaternary ammonium halides and bentonite; gelling inhibitors (when bentonite is present), such as siliconates; and bactericides.

The proportions in the present particulate compositions of the various required, preferred and optional components thereof will be such that the compositions made are effective laundry detergents which are especially useful in removing, with repeated washings, embedded particulate oily soils, which tend to give white and colored goods a dingy or tattletale gray appearance. Among such soils one of the most common and most difficult to remove is what is termed sebum/particulate soil, the soiling effects of which are closely mimicked by Spangler test soil, a well-known test soil employed in evaluations of cleaning abilities of detergent compositions. Improved removals of such soils and other stains are obtainable by washings with compositions of the present invention, even at such concentrations in wash waters as to result in low concentrations of enzymes, including cellulase, significantly below concentrations recommended in the art and by manufacturers of such enzymes.

The proportion of nonionic detergent in the invented compositions will normally be in the range of 4 to 30%, preferably 8 to 30%, more preferably 15 to 25%, and most preferably will often be about 17 or 20%. Such percentages are for phosphate and non-phosphate detergent compositions, and for bleaching and non-bleaching compositions, too.

The proportion of builder for the nonionic detergent will normally be in the range of 25 to 80%, preferably 40, 45 or 50 to 70 or 75%, and more preferably 55 to 65%. For non-bleaching, phosphate-containing detergent compositions the content of phosphate is normally in the range of 40 to 75%,

preferably 50 to 70%, e.g., about 59 or 60%, and usually it will be accompanied by 3 to 10% of sodium silicate, preferably 5 to 9% thereof, e.g., about 7%, which acts as a binder and bead strengthener, for spray dried compositions. For non-bleaching, non-phosphate detergent compositions the builder components will typically include 20 to 40% of zeolite, 15 to 40% of carbonate and 5 to 25% of bicarbonate, preferably 25 to 35% of zeolite, 20 to 30% of sodium carbonate and 5 to 15% of sodium bicarbonate, e.g., about 31% of Zeolite A, about 28% of sodium carbonate, and about 11% of sodium bicarbonate. For bleaching detergent compositions of the phosphate-built type the proportions of phosphate and silicate will normally be in ranges like those given for the non-bleaching compositions and similarly, for bleachings of non-phosphate compositions the proportions of zeolite, carbonate and bicarbonate will be like those given for the corresponding non-bleaching, non-phosphate compositions, but percentages will usually be decreased because of the presence of bleaching agent in the formulas, and sometimes zeolite content can even be lowered to 0.5 or 1%, and zeolite may even be eliminated from some formulas.

The cellulase contents of the present compositions will normally be in the range of 0.2 to 1% of the cellulase (as supplied, as Celluzyme® 1500T or cellulase of corresponding activity, as measured by CMC units). Preferably such content will be in the range of 0.3 to 0.7%, for example, about 0.5%. The proportions of protease and amylase will each normally be in the range of 0.1 to 2%, preferably 0.1 to 1%, e.g., about 0.3 to 0.5%, but in some instances the amylase may be omitted, which has been done when detergent compositions are of a bleaching type. In such cases therefore, the lower limits on the ranges of contents of amylase will be 0%. Other enzymes, such as lipase and carbohydroxyase, may also be present in the detergent compositions and the total proportion of non-cellulase enzymes (which may be only protease and amylase) will usually be within the range of 0.1 to 4%, preferably 0.2 to 2%, and more preferably 0.6 to 1%, with about equal proportions of each of the different enzymes being employed. However, when the detergent composition is also intended for use as a pre-soak, the proportions of all enzymes may be increased, sometimes to 2, 3 or even 10 times those given above, with proportions of other components being diminished accordingly.

Although the particulate detergent compositions of this invention are dry to the touch, non-caking and free flowing, they do contain some water, which often acts as a hydrating binder and helps to increase particle strengths. Normally the water content will be in the range of 1 to 15%, preferably 7 to 13%, e.g., about 10% for phosphate-containing nonionic detergent compositions of the non-bleaching type, made from spray dried base beads, and will normally be in the 1 to 15% range, preferably 4 to 10%, e.g., about 7%, for corresponding non-phosphate, non-bleaching products. For bleaching and other detergent compositions in which granular builders are often employed rather than spray dried builder beads, and in which other granular components may also be present, absorption of nonionic detergent and water is not as effective, and moisture contents may be less, such as within the range of 0.5% or 1 to 5%, preferably 1 to 3%, e.g., about 1%.

The proportion of PET-POET (called SRP for soil release promoting), when it is in these compositions, will normally be in the range of 0.3 to 4%, preferably 1.0 to 3.0%, e.g., about 1.5% or about 2%, and the content of sodium polyacrylate will usually be in the range of 0.01 to 2%, preferably 0.02 to 0.5%, e.g., about 0.05% or about 0.1%, with the polyacrylate content normally being from 3 to 100% or 4 to 10%, e.g., about 5% of the content of PET-POET copolymer. More SRP may be employed if desired, often up to 3 or 5 times as much, but economic constraints often limit the proportion present because this component is comparatively expensive. At the proportions given above, 0.3 to 4%, etc. the SRP is cost effective and its action in promoting soil release from laundry is satisfactory. The content of fluorescent brightener is normally in the range of 0.2 to 2%, preferably 0.3 to 1.5%, e.g., about 1%, on the basis of the brightener as supplied by the manufacturer, and such content applies to the total amounts of mixed fluorescent brighteners which may be utilized in the compositions.

When a per-compound oxygen bleach is present in the invented compositions the proportion thereof will usually be in the range of 10 to 35%, preferably being 10 or 20 to 30%, e.g., about 24%. When an activator to promote the release of bleaching oxygen from the per-compound is present it will normally be in amount from 0.2 to 5%, preferably 1 to 4%, e.g., about 3%, but the proportion thereof will depend on the particular activator or activator system employed.

Of course, various adjuvants may be utilized in different proportions to give the detergent composition certain properties or to improve its properties. Normally the total proportion of adjuvants (excluding fillers) will be in the range of 0.1 to 10%, preferably 0.5 to 5%, and more preferably 0.5 to 3%, it being considered that the lower the content of adjuvants in the present compositions the better, as a normal rule. The content of filler salts, such as sodium sulfate, will also normally be kept as low as feasible, usually being limited to 20%, preferably 10%, and more preferably 5%. However, under some circumstances, as when the detergent composition is of nonionic detergent, tripolyphosphate, cellulase, protease and amylase, and the

filler salt is sodium sulfate, as much as about 50% thereof may be used.

In American washing processes concentrations of the present compositions in the wash waters will be relatively low because the compositions will be highly concentrated. Thus, a normal charge of such compositions will be in the range of 0.04 to 0.08%, preferably 0.05 to 0.07%, e.g., about 0.06%. Proportions of individual components will normally be in the range of 0.005 to 0.02% of nonionic detergent, 0.03 to 0.06% of total builders for such nonionic detergent, 0.00005 to 0.0008% of protease, 0 or 0.00005 to 0.0008% of amylase, and 0.0001 to 0.0008% of cellulase. Using CMC units/liter, preferably 3 to 7 CMC units/liter, e.g., about 4.7 or 5 CMC units/liter, may be present in the wash water in typical cases.

The present compositions, sometimes with increased proportions of cellulase and other enzymes present, as mentioned elsewhere herein, may be used as a pre-soak, before washing, or as a soaking detergent, and satisfactorily remove various stains, including oily sebum stains, from laundry, especially from cottons and cotton-containing blends. In such pre-soak or soak tests, after the laundry is soaked in the detergent solution it is subjected to a single wash, using the soak solution as a source of detergent composition, and is rinsed and dried. Cleaning results from such soak tests are relatable to and indicative of the power of the composition to remove hard to remove, deep soils from laundry in repeated launderings, and in both washing and soaking operations the presence of the cellulase significantly improves cleaning by nonionic detergent compositions more than it improves cleaning by anionic detergent compositions.

The invented detergent compositions can be manufactured by techniques similar to those employed for making known commercial detergent compositions. Either phosphate or non-phosphate non-bleaching compositions may be made by spray drying an aqueous crutcher mix of builders to hollow bead form and then applying melted, normally solid nonionic detergent to such beads, while mixing them, so that the nonionic detergent penetrates into the bead interiors, while also at least partially coating external surfaces of the beads. In some instances other components of the detergent composition may be included in the melt of nonionic detergent, such as PET-POET copolymer and polyacrylate. Additional components of the detergent compositions may be post-added to the built detergent beads and such post-additions may be utilized to increase the bulk density of the detergent compositions, which is intentionally made highly concentrated, often being of a bulk density of at least 0.7 g./ml as in the range of 0.7 to 1.0 g./ml. Preferably, the enzymes are prilled and are blended with the beads, after which any perfume to be present may be sprayed onto the moving mix, as essentially the last manufacturing operation. Normally, the fluorescent brightener will be stable enough to withstand spray drying so it will be included with the builders in the crutcher mix. Other stable components of the compositions may also be included in the crutcher mix and those which are unstable in heated aqueous media or cannot withstand the temperature of the spray drying air (usually 200 to 500 °C.) may be post-added, either as particulate or liquid materials. Because per-compounds that may be employed as bleaching components in the invented compositions are unstable under such conditions, they will normally be post-added.

To wash with the invented compositions one needs only employ them in the same manner in which other laundry detergents are used. Normally they will be charged to wash waters in washing machines and such waters will typically be of hardnesses in the range of 0 to 400 parts per million, as CaCO₃, usually being within the range of 50 to 300 p.p.m., such as 100 to 200 p.p.m. While the amount of detergent composition employed may depend to some extent on preferences of users and dirtiness of the laundry, normally the concentration of detergent composition in the wash water will be on the order of 0.04% to 2%, depending on the type of washing and the machine employed. In European washing machines, which utilize hotter and more concentrated (in detergent content) wash waters, the detergent composition content will often be in the range of 0.3 to 1.5% or more, whereas in typical American practice it will usually be in the range of 0.05 or 0.1 to 0.2 or 0.3%. Wash water temperatures may span the range of 10 to 90 or 95 °C., often being in the ranges of 10 to 40, 50 or 60 °C., for American practice, and even as low as 10 to 30 °C., whereas in European practice such range can be from 30 or 40 to 80, 90 or 95 °C., and sometimes 40 to 60 °C. (in recent years European wash water temperatures have been lowered somewhat to save energy and to allow automatic washing of laundry dyed with more sensitive dyes).

After normal automatic washing of soiled laundry it will usually be subjected to drying in an automatic laundry dryer but sometimes line drying or open air drying may be practiced instead. During the drying process or during rinse operations fabric softening agents may be applied to the laundry or such may be included in the detergent composition or in the wash water, and may be applied during the washing operation.

During washing and during any other processing of the laundry in which cellulase is brought into contact with the fibers of the laundry, specifically cotton fibers thereof or blends of cotton and polyester, the cellulase, in addition to helping to break down some soils derived from vegetable matter, also acts in a subtle manner, in concert with other composition components, to modify the nature of such fiber surfaces. It

has been noted that such actions on the cotton fibers remove microscopic sized ragged edges from the fibers, which tend to hold dirt and stains, so that otherwise such soils would not be readily removed by normal washing. Usually the cellulase employed in the past has been bacterial cellulase and was used in anionic detergent compositions at substantially higher concentrations than are employed in accordance with the present invention. Because enzymatic activity tends to increase with increasing temperature, wash waters employed were normally hot, and because the enzymes were considered to be pH-sensitive, detergent compositions employed were held at pH's near neutral. When using relatively high concentrations of cellulase in anionic detergent compositions under such conditions improved cleaning of hard to remove stains was noted and at the same time, apparently due to the same type of effect of the cellulase on cotton fibers, the fibers, fabrics and laundry became softer to the touch, presumably because of the increased smoothness of the fibers after the action of the cellulase on them. Thus, deep cleaning and fabric softening both resulted from the described treatment of cotton fabrics with cellulase in the wash water, and apparently such results were intimately related to the identity of the detergent composition and to the action of the cellulase on the cotton fibers.

The present invention differs from prior art laundry detergent compositions and processes because the cellulase very preferably employed is such as may be derivable from fungi. Good activity of the cellulase is obtained, using the invented compositions, which improve the removal of embedded or ingrained dirt, stains and soils, which are difficult to remove from laundry and which often give it a grayish cast, even after a plurality of washings. Such grayness is significantly diminished, especially after plural washings, despite the alkalinity of the wash water, and such removal of this hard-to-remove soil is even effectable at comparatively low temperatures, such as those in the 10 to 40° C. range. Furthermore, such improvements are obtained, compared to a control not containing cellulase, even when low concentrations of fungal cellulase are present in the wash water, such as those in the range of 1.5 to 12 CMC units/liter, e.g., about 4 to 5 CMC units/liter. Surprisingly, such improvements are not obtained when the same proportion of such cellulase is added to a comparable commercial anionic detergent composition, such as that sold under the trademark FAB®, when such modified product is tested in the same manner. This phenomenon, observed by applicants, is also different from activities of prior art detergent compositions that have been reported, because there is no corresponding improvement in fabric softening, which has been mentioned as another effect of cellulase on laundry. In other words the present compositions appear to be different in properties from what might have been expected from the prior art because the prior art, which related primarily to anionic detergent compositions, indicated that at the higher concentrations employed its detergent compositions would both clean and soften, which is not the case for the invented compositions. Thus, it appears that the presence of the unexpectedly beneficial cleaning effect and the absence of softening are indicative of unobviousness of the present novel compositions.

In efforts to evaluate the ability of the present detergent compositions and variations thereof to remove internal soils from fabrics such fabrics have been stained with oily, difficultly removable soils, including Spangler sebum soil, which is considered to closely duplicate natural combinations of sebum and oily soils that are found on normal household laundry, especially on shirt collars and cuffs, which are considered among the more difficult laundry items to "deep" clean. In some instances laundry swatches were stained with a variety of set-in oily and particulate soils, including clay, blood, liquid make-up, blueberry pie filling, grass and Spangler soils, and these and EMPA 101 swatches were tested. Reflectometer readings were taken after washings and dryings, often repeated, and changes in whiteness of the swatches were recorded. Statistical analyses of such data established whether the changes were significant or not. From such tests it could be determined whether a formula was effective against certain stains, and its overall effectiveness against a variety of such soils could also be assessed. Although such tests are useful they are very time consuming and labor intensive so efforts were made to develop other tests which would be indicative of long term effects of employing particular detergent compositions to wash and whiten household laundry. It was found that it was possible to obtain essentially the same types of results if instead of employing multiple washings of stained test fabrics, such stained fabrics were soaked at about room temperature for one hour in a highly concentrated aqueous solution of the detergent composition, followed by a single washing and drying. For example, instead of charging 40 grams of the detergent composition of this invention to a 64 liter wash tub of an automatic washing machine the 40 grams of detergent composition were mixed with one liter of water at room temperature and the soiled swatches to be tested by this soaking technique were soaked in the detergent composition solution for an hour, after which they were washed, rinsed and dried, and were read on a reflectometer. By such testing and back-up testing it was established that the present low cellulase level compositions are surprisingly effective in the described built nonionic detergent compositions based on NRE nonionic detergents. The improved whitening of the laundry that results is not something which can be measured only instrumentally, as by reflectometer; the benefits

obtained are also visible to the naked eye, especially after repeated launderings of cotton swatches that were initially soiled with Spangler soil. After such washings the swatches appear to the eye to be definitely whiter than identically soiled swatches washed with control detergent compositions of the same formulas as the experimental compositions, but without cellulase. It should be understood that even after repeated
5 launderings of the stained swatches they still show some of the stains applied to them initially. That is because the stains are applied by methods that involve heat setting them, which is more severe than normal stainings. However, repeated washings continue to remove more of the stains and to lower the background staining or dinginess. The results of such washings have been found to be comparable to those obtained in normal repeated soilings and washings. Even more surprisingly, it has been found that soaking
10 test results are similarly relatable to results of such repeated normal soilings and washings. Thus, such types of tests may be used to measure effectiveness of a detergent composition in removing hard-to-remove soils and in avoiding dingy or grayish appearances of washed items after soiling ar repeated launderings.

The following examples illustrate but do not limit the invention. Unless otherwise mentioned, all parts
15 and percentages are by weight in these example, this specification and the appended claims, and all temperatures are in °C.

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EXAMPLE 1

	<u>Component</u>	<u>Percent (by weight)</u>
5	Sodium tripolyphosphate	59.3
	* Narrow range ethoxylate nonionic detergent	20.0
	Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$)	7.0
10	** Celluzyme [®] 1500T, prilled, mfd. by Novo Industri A/S	0.5
	*** Proteolytic enzyme (Alcalase [®])	0.3
15	*** Amylolytic enzyme (Termamyl [®])	0.3
	+ PET-POET copolymer	1.90
	+ Sodium polyacrylate	0.10
20	Distilbene type fluorescent brightener (Tinopal 5BM)	1.0
	Water	9.0
25	Perfume	0.2
	Adjuvants	q.s.
30		100.0
35	* Tergitol [®] 24-L-60N, manufactured by Union Carbide Corporation (a NRE condensation product of mixed C_{12} and C_{14} linear alcohols and 7 moles of ethylene oxide per mole)	
40	** Source of fungus-derived cellulase (1500 CMC units/gram)	
	*** Prilled together	
45	+ Fused together, supplied as Alkaril SRP-2-F, 95% of PET-POET copolymer of weight average molecular weight of about 40,000 and 5% of sodium polyacrylate of molecular weight of about 2,000)	
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The detergent composition of the above formula is made by spray drying an aqueous crutcher mix (50-60% solids content) of sodium tripolyphosphate, sodium silicate and fluorescent brightener in a conventional spray drying tower, with drying air at temperatures in the range of 200 to 450° C., to spray dried hollow beads of moisture content of about 13% and particle sizes in the range of No's. 10-100, U.S. Sieve Series. After cooling of these base beads the nonionic detergent, in molten form, at a temperature in the range of 50 to 60° C., is sprayed onto the beads, is absorbed by them, coats surfaces thereof and solidifies thereon. Subsequently, there are mixed with the resulting detergent composition the prilled enzymes and

the SRP-2-F, after which the perfume is sprayed onto the product. The result is a free flowing heavy duty nonionic laundry detergent composition of about 10% moisture content, which is then tested for cleaning power against laundry items containing hard to remove sebum soil, compared to a control composition of the same formula except for the omission of the cellulase (which may be compensated for by proportional increases in the other components).

When cotton swatches are stained with Spangler sebum/particulate soil and are washed in an automatic washing machine with the experimental and control compositions at 0.06% concentration or 4.5 CMC units/liter in wash water at a pH of 8.5 and a temperature of 49° C., measurable improvements in removal of such soils are noted for the experimental, compared to the control, and such improvements in stain removal remain measurable after subsequent washes. After three and five such washes Rd values increase, indicating that the invented detergent composition is releasing strongly held soil from the laundry, which soil remained after the initial washing. In comparable tests, utilizing a leading commercial anionic laundry detergent composition, to which the same proportion of such cellulase had been added, after repeated washings the swatches washed with such experimental composition were not significantly better than the controls.

The mentioned tests are also repeatable with essentially the same results being obtained when the experimental and control formulas are compared by soaking, for an hour, of cotton swatches which had been stained in the same manner, in 4% concentration solutions of the respective detergent products in water at 49° C. or at room temperature (with the pH being about 9), and subsequently washing, rinsing and drying the swatches, and measuring the reflectances thereof.

In a variation (designated 1A) of the formula of this example the phosphate-built nonionic detergent is made by utilizing different proportions of some components, so that the final product comprises 59.2 parts of the sodium polyphosphate, 7.0 parts of the sodium silicate, 20.0 parts of the NRE nonionic detergent, 1.0 part of a co-primed mixture of about equal proportions of proteolytic and amylolytic enzyme, 2.0 parts of the PET-POET - polyacrylate mix (SRP-2-F), 1 part of the fluorescent brightener, 0.2 part of perfume, 9.1 parts of water and 0.5 part of Celluzyme 1500T. The product is made in essentially the same manner as previously described and two further variations and the principal variation formula (1A) are compared to a leading commercial anionic detergent in soaking tests, as previously described, using 40 grams of each product per liter. In one of the variation formulas (1A0) no cellulase was present in the composition and in the other (1A1) the proportion had been increased to 1%. The zero content cellulase formula was measurably inferior to the commercial product in removing Spangler soil from cotton by soak test whereas the 1% cellulase formula was clearly superior to such commercial detergent.

In similar tests the composition of Formula 1A was compared to a composition which did not contain cellulase (1A0). The cotton test swatches used had previously been stained with Spangler sebum/particulate soil, liquid make-up, Piscataway (New Jersey) clay and EMPA 101 oily soil. Composition 1A, containing 0.5% of cellulase, was significantly superior, on average, to that without cellulase (1A0) in removing such soils from the swatches and such improvements were even more significant with respect to the Spangler, EMPA and make-up soils than with respect to the clay soil, in these experiments.

The experimental composition mentioned, 1A, and similar control composition 1A0, without cellulase, were tested further, using five washings of stained cotton swatches at 49° C., each being compared to the commercial detergent, with the test stains being grass and Spangler sebum/particulate soils, both on cotton. In some instances a heavy soil load was applied to the cotton and the swatches were in a large size laundry load, and in other instances light soil was applied and the swatches were in a medium size laundry load. In both situations the cellulase-containing composition removed the soil better than the composition containing no cellulase. Such washing machine tests were all run at a concentration of 40 grams of detergent composition per 64 liters of wash water, which is about 0.06%, so that the cellulase concentration for 1A was about 0.0003% or 4.7 CMC units/liter, in the wash water.

In soaking tests of the type described the same nonionic detergent composition (1A), with 0.5% cellulase in the formulation, was tested against a control composition (1A0), without cellulase, and was found to be significantly more effective in removing EMPA 101, blood, liquid make-up, blueberry pie and grass stains from cotton swatch substrates. It was also more effective in removing clay and Spangler stains but the extents of such removals were not considered as significant in this test. In a similar pair of tests, with and without 0.5% of cellulase in an anionic detergent composition, consisting of 20% of sodium linear tridecylbenzene sulfonate, 44% of sodium tripolyphosphate, 10% of soda ash, and 5% of sodium silicate, with the balance being water and adjuvants, no significant improvements in cleaning were noted for the cellulase formulation with respect to the test stains and the cleaning improvements noted were less than the improvements obtained with the nonionic detergent compositions that incorporated cellulase. Essentially the same types of results obtained when the Alkaril SRP-F-2 content of the nonionic composition was doubled.

EXAMPLE 2	
Component	Percent (by weight)
Sodium zeolite (Zeolite A)	30.5
Sodium carbonate	28.0
Sodium bicarbonate	11.0
Narrow range ethoxylate nonionic detergent	20.0
*** Celluzyme 1500T, prilled	0.5
*** Proteolytic enzyme (Alcalase)	0.3
*** Amylolytic enzyme (Termamyl)	0.3
+ PET-POET copolymer	1.90
+ Sodium polyacrylate	0.10
Distilbene type fluorescent brightener (Tinopal 5BM)	1.0
Water	5.9
Perfume	0.2
Adjuvants	q.s.
	100.0

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The product of this example is of spray dried base beads having nonionic detergent absorbed in them. The base beads are made by the spray drying process described in Example 1, with the crutcher mix being of zeolite, carbonate, bicarbonate and distilbene type fluorescent brightener in about a 50% aqueous slurry. Because bicarbonate decomposes to carbonate during spray drying, to the extent of 1/3 to 1/2 of the bicarbonate charged, an appreciable proportion of the carbonate of the formula derives from charged bicarbonate (in the crutcher mix approximately equal proportions of carbonate and bicarbonate are initially present). The spray dried base beads are of the same particle size range as the base beads of Example 1 and are of a moisture content of about 9%. The other components are absorbed by, admixed with or sprayed onto the base beads to form the final free flowing non-phosphate built product. When such product is tested for cleaning power in multiple washings of laundry items stained with hard to remove or "difficult" soils, which include sebum soil, and is compared to a control composition of the same formula except for the omission of the cellulase, improvements in removals of such soils in washings after the initial washing are noted, indicating that the deep down or internal soil is being washed out of the test pieces, which after such multiple washings, do not appear to the human eye to be as stained as the controls. Such effects are obtained to greater extents at medium or high temperatures, such as 49 °C., with 3 to 5 washings, and are obtainable despite the facts that the wash water pH may be in the range of 9 to 9.5, and that the concentrations of the detergent composition and of the contained cellulase are low, on the order of 0.04 to 0.08% for the detergent composition and 0.0002 to 0.0004% for the cellulase (as supplied). As with the phosphate detergent compositions of this invention, the cleaning power of the non-phosphate detergent composition of this example against hard-to-remove soils, such as clay, grass, liquid make-up, oily soil (EMPA-101) and test fabrics soil, especially in wash water at higher temperatures, such as 49 °C., is notable and surprisingly good.

In a relatively minor variation of the formula of this example the proportion of SRP-2-F was increased to 2% and the moisture content was decreased to 5.9%. This formula product, designated 2A, was tested by the pre-soak test against a non-phosphate built commercial detergent composition using a 4% concentration, one hour soak at 49 °C. Reflectometer readings show this composition to be significantly better than the commercial detergent product in removal of Spangler soil and in removing the soil from EMPA 101 test swatches. It was also very effective in removing blueberry pie stain from cotton. When a similar formula was made (2A0) which did not include any cellulase, such differences versus the commercial detergent were not obtained. Thus, the invented compositions are clearly superior to a prior art commercial detergent composition that does contain cellulase, and such results are obtainable even at higher pH's, comparatively low washing temperatures, and at low concentrations of detergent composition and of cellulase in the wash water. The reported results in this example and Example 1 are obtainable when utilizing as a control a commercial heavy duty detergent composition such as that sold under the trademark FAB but similar results are obtainable when other competitive particulate heavy duty detergent compositions are compared to the invented products.

EXAMPLE 3	
Component	Percent (by weight)
Sodium tripolyphosphate	51.0
Sodium metasilicate	6.0
• Nonionic detergent	12.0
Sodium perborate monohydrate	22.5
Perborate activator (TAED)	2.5
Stilbene fluorescent brightener (Tinopal 5BM)	0.5
Sodium ethylene diamine tetraacetate (EDTA)	0.4
Sodium carboxymethyl cellulose (CMC)	1.5
Lower alkyl phosphoric ester	1.0
Proteolytic enzyme (Alcalase)	0.5
Cellulase, fungal (1500 CMC units/g.)	0.5
Water	1.0
Zeolite A powder	0.6
	100.00
• C ₁₂₋₁₅ alcohol (7 EtO) nonionic detergent (BRE type)	

The above formula is made by mixing components thereof, which are mostly in powder form, and spraying a liquid state nonionic detergent onto such mix. A small proportion of powdered zeolite, usually No. 200 sieve Zeolite 4A, is then added, which has the effect of improving flowability of the grand composition.

The above formula is of a bleaching particulate detergent composition intended for European use. When phosphates are barred from detergent compositions the phosphate and silicate contents may be replaced by zeolite, carbonate and bicarbonate, in the same proportions employed in the first formula of Example 2.

Both the phosphate and non-phosphate bleaching formulas of this example are effective detergent compositions under normal European washing conditions, which were mentioned earlier, and serve to remove deeply embedded soils from laundry, especially cotton items. Additionally, they help to prevent new laundry items from becoming grayed due to soils penetrating to the interiors of fibers thereof during repeated soilings and washing operations. Such results are verifiable by multiple washing tests and by the soak test, as previously described.

The cleaning power of this formulation can be improved by replacing the BRE nonionic detergent with the NRE nonionic detergent of Example 1 or by replacing it with comparable Shell Chemical Company NRE nonionic detergents, as mentioned in the specification. If the perborate and perborate activator are removed from the formulations the desirable oxygen bleaching action thereof is lost but still the presence of the cellulase helps to remove hard to remove soils from test swatches during repeated launderings.

EXAMPLE 4

In repeated sets of experiments, there were tested phosphate-built nonionic detergent, phosphate-built anionic detergent, non-phosphate-built nonionic detergent and non-phosphate-built anionic detergent, after 1, 3 and 5 washings with wash water at 21° C. and 49° C., using eight different standard stains (clay, Spangler, EMPA 101, blood-milk-ink, liquid make-up, blueberry, grass and black ink) each on cotton except the black ink, which is on 65:35 polyester:cotton. In such experiments soak tests were also employed to compare the stain removing actions of the described compositions. The formulas of the tested compositions follow.

Formula 4A	
(Phosphate-Built Nonionic Detergent Composition)	
Component	Percent (by weight)
Nonionic ethoxylated alcohol (NRE, as in Example 1)	20.0
Sodium tripolyphosphate	59.3
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$)	7.0
Tinopal 5BM	1.0
Dual enzyme (protease/amylase, 1:1)	1.0
Celluzyme 1500T	0.5
Water	q.s.
	100.00

Formula 4B	
(Non-Phosphate Nonionic Detergent Composition)	
Component	Percent (by weight)
Nonionic ethoxylated alcohol (NRE, as in Ex. 1)	20.0
Sodium aluminium silicate (Zeolite A)	30.5
Sodium carbonate	28.0
Sodium bicarbonate	11.0
Tinopal 5BM	1.0
Dual enzyme (protease/amylase, 1:1)	1.0
Celluzyme 1500T	0.5
Water	q.s.
	100.00

Formula 4C	
(Phosphate-Built Anionic Detergent Composition)	
Component	Percent (by weight)
Linear tridecylbenzene sulfonate, sodium salt	16.6
Sodium tripolyphosphate	29.7
Sodium sulfate	35.8
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$)	7.4
Tinopal 5BM	0.2
Hydroxypropyl methyl cellulose	0.6
Sodium carboxymethyl cellulose	0.1
Celluzyme 1500T	0.5
Water	9.1
	100.00

Formula 4D	
(Non-Phosphate Anionic Detergent Composition)	
Component	Percent (by weight)
Linear tridecylbenzene sulfonate, sodium salt	17.6
Sodium aluminium silicate (Zeolite A)	25.2
Sodium carbonate	22.7
Sodium sulfate	16.4
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$)	5.3
Tinopal 5BM	0.2
Hydroxypropyl methyl cellulose	0.6
Sodium carboxymethyl cellulose	0.1
Sodium polyacrylate (M.W. = 40,000 $\pm$ 10,000)	2.1
Celluzyme 1500T	0.5
Water	9.3
	100.00

Formulas 4A and 4B include 0.5% of Celluzyme 1500T, or 7.5 CMC units per gram. Thus, when in the described washing tests 40 g. of such detergent compositions are charged to 64 liters of wash water the cellulase concentration in the wash water is 4.7 the units/ liter. Formulas 4C and 4D include 0.5% of Celluzyme 1500T, or 7.5 CMC units per gram, too. In the described washing tests when such formulas are tested 80 g. of detergent composition are charged to 64 liters of wash water and the cellulase concentration in the wash water is 9.4 CMC units/liter "Control" formulas are identical with the experimental formulas except for the omissions of Celluzyme 1500T and the replacements thereof with sodium sulfate in the anionic formulas, with sodium tripolyphosphate in the control corresponding to Formula 4A, and with Zeolite A in the control corresponding to Formula 4B. The controls are designated 4A0, 4B0, 4C0 and 4D0, respectively.

Differences in Rd (reflectance) readings before and after one, three and five washes, compared to stained, unwashed swatches (averages of readings on eight swatches) were calculated for the cellulase-containing compositions and for the non-cellulase "controls" and it was found that for the phosphate-built nonionic detergent composition (4A) after three and after five washes improved cleaning compared to such control 4A0 was statistically significant at both 21°C. and 49°C. washing temperatures. For the non-phosphate nonionic formula (4B) statistically significant cleaning, compared to 4B0 was obtained after five wash cycles at 49°C. Formula 4C was not statistically better in stain removal than Formula 4C0 and 4D was statistically better than 4D0 only for two stains at five washes at 49°C., much less than the improvement of 4B over 4B0. In soak tests the 4A formula is statistically superior to 4A0 and the 4C formula was no better than 4C0.

This example establishes that even without the presence of PET-POET soil releasing copolymer in the formulas the present built nonionic detergent compositions containing cellulase remove hard to remove soils and stains better than controls that do not contain such cellulase, and the presence of cellulase in the nonionic compositions improves their cleaning power more than does a similar proportion in anionic detergents.

The various detergent compositions described in the above working examples may be packaged in normal detergent cartons or may be sealed inside pre-measured, single-use pouches which either dissolve in the wash water or allow the detergent composition to penetrate the walls thereof during the washing operation. If desired, the compositions may be employed as pre-soaks, as has been indicated by the successful reports of results of the soak tests mentioned in the Examples.

The invention has been described with respect to illustrations, embodiments and examples thereof, but is not to be limited to these because it is evident that one of skill in the art with the present specification before him will be able to utilize substitutes and equivalents without departing from the invention.

Claims

1. A heavy duty particulate synthetic organic nonionic detergent composition which has significantly

improved cleaning action against hard to remove soils in laundry fibers, which comprises 4 to 30% of synthetic organic nonionic detergent, 25 to 80% of builder for such nonionic detergent, 0.1 to 2% of protease, 0 to 2% of amylase, 0.2 to 1% of cellulase, and 1 to 15% of water.

2. A particulate detergent composition according to claim 1 in which the builder is selected from the group consisting of polyphosphates, silicates, carbonates, bicarbonates, borates, citrates, NTA, polyacetal carboxylates and zeolites, and mixtures thereof, in which the cellulase is of a type derived from fungus, and which comprises 0.3 to 4% of polyethylene terephthalate-polyoxyethylene terephthalate soil release promoting copolymer (PET-POET).

3. A particulate detergent composition according to claim 2 wherein the nonionic detergent is of narrow range ethoxylate (NRE) type, which is a condensation product of an alcohol of 10 to 18 carbon atoms with an average of 5 to 10 moles of ethylene oxide, with at least 70% of the ethylene oxide thereof being in alcohol ethoxylates of 4 to 12 ethylene oxide groups per mole, the builder consists essentially of 40 to 75% of sodium polyphosphate and 3 to 10% of sodium silicate, the enzymes consist essentially of 0.1 to 0.1% of protease, 0.1 to 1% of amylase and 0.3 to 0.7% of cellulase, the PET-POET copolymer is of a weight average molecular weight in the range of 15,000 to 50,000, and the proportion of such PET-POET copolymer is in the range of 1.0 to 3.0%.

4. A particulate detergent composition according to claim 3 which comprises 15 to 25% of NRE detergent which is a condensation product of a higher primary or secondary alcohol and ethylene oxide, with the ethylene oxide being in polyethoxy groups averaging 6 to 9 ethylene oxide groups per mole and with at least 70% of the ethylene oxide being in higher fatty alcohol ethoxylates of 5 to 10 ethylene oxide groups per mole, 50 to 70% of sodium tripolyphosphate, 5 to 9% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.6 to 1:3, 0.1 to 1% of protease, 0.1 to 1% of amylase, 0.3 to 0.7% of cellulase, 1.5 to 2.0% of PET-POET copolymer, the weight average molecular weight of which is in the range of 19,000 to 43,000 and the molecular weight of the polyoxyethylene of which is in the range of 1,000 to 10,000, 0.01 to 2% of polyacrylate, 0.2 to 2% of fluorescent brightener, of the stilbene type, and 7 to 13% of water.

5. A particulate detergent composition according to claim 4 which comprises about 20% of NRE nonionic detergent which is a condensation product of a higher saturated fatty alcohol of 12 to 14 carbon atoms with 5 to 10 moles of ethylene oxide, in which at least 85% of the ethylene oxide is in higher fatty alcohol ethoxylates of 5 to 10 moles of ethylene oxide per mole of such nonionic detergent, about 59% of sodium tripolyphosphate, about 7% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4, about 0.3% of protease, about 0.3% of amylase, about 0.5% of cellulase, about 1.9% of PET-POET copolymer, of weight average molecular weight of about 40,000, about 0.1% of sodium polyacrylate, of molecular weight of about 2,000, about 1% of distilbene type fluorescent brightener and about 10% of water.

6. A particulate detergent composition according to claim 5 wherein the protease, amylase and cellulase are present in prilled form, the sodium tripolyphosphate, sodium silicate and distilbene brightener are in spray dried bead form and the nonionic detergent is in solid form coating such spray dried beads and interior surfaces thereof.

7. A particulate detergent composition according to claim 1 which is of non-phosphate type, in which the builder is selected from the group consisting of carbonates, bicarbonates, borates, citrates, NTA, polyacetal carboxylates and zeolites, and mixtures thereof, and in which the cellulase is of a type derived from fungus.

8. A particulate detergent composition according to claim 7 which comprises 0.3 to 4% of PET-POET soil release promoting copolymer of weight average molecular weight in the range of 15,000 to 50,000, and wherein the nonionic detergent is of narrow range ethoxylate (NRE) type, which is a condensation product of an alcohol of 10 to 18 carbon atoms with an average of 5 to 10 moles of ethylene oxide, with at least 70% of the ethylene oxide thereof being in alcohol ethoxylates of 4 to 12 ethylene oxide groups per mole, the builder is a builder system which consists essentially of 20 to 40% by weight of the composition of zeolite, 15 to 40% of sodium carbonate and 5 to 25% of sodium bicarbonate, and the enzymes consist essentially of 0.1 to 1% of protease, 0.1 to 1% of amylase and 0.3 to 0.7% of cellulase.

9. A particulate detergent composition according to claim 8 which comprises 15 to 25% of NRE detergent which is a condensation product of a higher primary or secondary alcohol and ethylene oxide, with the ethylene oxide being in polyethoxy groups averaging 6 to 9 ethylene oxide groups per mole and with at least 70% of the ethylene oxide being in higher fatty alcohol ethoxylates of 5 to 10 ethylene oxide groups per mole, 25 to 35% of zeolite, 20 to 30% of sodium carbonate, 5 to 15% of sodium bicarbonate, 0.1 to 1% of protease, 0.1 to 1% of amylase, 0.3 to 0.7% of cellulase, 1.0 to 3.0% of PET-POET copolymer, the weight average molecular weight of which is in the range of 19,000 to 43,000, and the molecular weight of the polyoxyethylene of which is in the range of 1,000 to 10,000, 0.02 to 0.5% of polyacrylate, 0.2 to 2% of fluorescent brightener, which is of a stilbene type, and 4 to 10% of water.

10. A particulate detergent composition according to claim 9 which comprises about 20% of NRE nonionic detergent which is a condensation product of a higher saturated fatty alcohol of 12 to 14 carbon atoms with 5 to 10 moles of ethylene oxide, in which at least 85% of the ethylene oxide is in higher fatty alcohol ethoxylates of 5 to 10 moles of ethylene oxide per mole of such nonionic detergent, about 31% of sodium zeolite, about 28% of sodium carbonate, about 11% of sodium bicarbonate, about 0.3% of protease, about 0.3% of amylase, about 0.5% of cellulase, about 1.9% of PET-POET copolymer, about 0.1% of sodium polyacrylate of molecular weight of about 2,000, about 1% of distilbene type fluorescent brightener and about 7% of water.

11. A particulate detergent composition according to claim 10 wherein the protease, amylase and cellulase are present in prilled form, the sodium zeolite, sodium carbonate, sodium bicarbonate and distilbene brightener are in spray dried bead forms, and the nonionic detergent is in solid form, coating such spray dried beads and interior surfaces thereof.

12. A particulate detergent composition according to claim 1 which is of bleaching type, which comprises 10 to 35% of perborate bleach and in which the cellulase is of a type derived from fungus.

13. A particulate bleaching detergent composition according to claim 12 wherein the nonionic detergent is of narrow range ethoxylate (NRE) type, which is a condensation product of an alcohol of 10 to 18 carbon atoms with an average of 5 to 10 moles of ethylene oxide, with at least 70% of the ethylene oxide thereof being in alcohol ethoxylates of 4 to 12 ethylene oxide groups per mole, the builder consists essentially of 40 to 75% of sodium polyphosphate and 3 to 10% of sodium silicate, the enzymes consist essentially of 0.1 to 1% of protease, 0.1 to 1% of amylase and 0.3 to 0.7% of cellulase, and the perborate bleach is sodium perborate and is 10 to 35% of the composition.

14. A particulate bleaching detergent composition according to claim 13 which comprises about 12% of NRE nonionic detergent which is a condensation product of a higher saturated fatty alcohol of 12 to 14 carbon atoms with 5 to 10 moles of ethylene oxide, in which at least 85% of the ethylene oxide is in higher fatty alcohol ethoxylates of 5 to 10 moles of ethylene oxide per mole of such nonionic detergent, about 52% of sodium tripolyphosphate, about 6% of sodium silicate, about 0.5% of protease, about 0.5% of cellulase, about 24% of sodium perborate monohydrate, about 3% of perborate activator, about 0.5% of distilbene type fluorescent brightener and about 1% of water.

15. A particulate bleaching detergent composition according to claim 12, of non-phosphate type, wherein the nonionic detergent is of narrow range ethoxylate (NRE) type, which is a condensation product of an alcohol of 10 to 18 carbon atoms with an average of 5 to 10 moles of ethylene oxide, with at least 70% of the ethylene oxide thereof being in alcohol ethoxylates of 4 to 12 ethylene oxide groups per mole, the builder consists essentially of 5 to 40% of zeolite, 15 to 40% of sodium carbonate and 5 to 25% of sodium bicarbonate, the perborate bleach is sodium perborate and is 10 to 30% of the composition, and the enzymes consist essentially of 0.1 to 1% of protease, 0.1 to 1% of amylase and 0.3 to 0.7% of cellulase.

16. A particulate bleaching detergent composition according to claim 15 which comprises about 12% of NRE nonionic detergent which is a condensation product of a higher saturated fatty alcohol of 12 to 14 carbon atoms with 5 to 10 moles of ethylene oxide, in which at least 85% of the ethylene oxide is in higher fatty alcohol ethoxylates of 5 to 10 moles of ethylene oxide per mole of such nonionic detergent, about 26% of zeolite, about 23% of sodium carbonate, about 9% of sodium bicarbonate, about 24% of sodium perborate monohydrate, about 0.5% of protease, about 0.5% of cellulase, about 3% of perborate activator, about 0.5% of distilbene type fluorescent brightener and about 1% of water.

17. A process for washing laundry which has hard-to-remove soils in the fibers of the fabrics thereof and for significantly removing such hard to remove soils from the laundry fabrics which comprises washing such laundry at a temperature in the range of 10 to 90° C. in wash water which contains synthetic organic nonionic detergent, builder for such nonionic detergent, protease, and cellulase derived from fungus, which components are at concentrations corresponding to those in 0.04 to 2% concentrations in the wash water of a particulate composition described in claim 1, with the cellulase concentration in the wash water being in the range of 1.5 to 12 CMC units/liter.

18. A process according to claim 17 wherein a particulate detergent composition is the source of the nonionic detergent, builder, protease, amylase and cellulase, and such detergent composition is in accordance with the description thereof in claim 3, the wash water temperature is in the range of 10 to 60° C., the detergent composition concentration in the wash water is in the range of 0.05 to 0.2%, and the cellulase concentration in the wash water is in the range of 3 to 10 CMC units/liter.

19. A process according to claim 17 wherein a particulate detergent composition is the source of the nonionic detergent, builder, protease, amylase and cellulase, and such detergent composition is in accordance with the description thereof in claim 8, the wash water temperature is in the range of 10 to 60° C., the detergent composition concentration in the wash water is in the range of 0.05 to 0.2%, and the

cellulase concentration in the wash water is in the range of 3 to 10 CMC units/liter.

20. A process according to claim 17 wherein the particulate detergent composition is the source of the nonionic detergent, builder, protease, amylase and cellulase, and such detergent composition is in accordance with the description thereof in claim 13, the wash water temperature is in the range of 40 to 95° C., the detergent composition concentration in the wash water is in the range of 0.3 to 1.5%, and the cellulase concentration in the wash water is in the range of 3 to 10 CMC units/liter.

21. A process according to claim 17 wherein the particulate detergent composition is the source of the nonionic detergent, builder, protease, amylase and cellulase, and such detergent composition is in accordance with the description thereof in claim 15, the wash water temperature is in the range of 40 to 95° C., the detergent composition concentration in the wash water is in the range of 0.3 to 1.5%, and the cellulase concentration in the wash water is in the range of 3 to 10 CMC units/liter.

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