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 **Heavy duty laundry detergent compositions of reduced dye transfer properties.**

 A heavy duty particulate laundry detergent composition which is of reduced dye transfer properties and improved dye stability during laundering of mixed colored and white fabric laundry items is a built nonionic detergent composition (with the builder usually including sodium tripolyphosphate and/or zeolite) in which bentonite or other suitable montmorillonite clay adsorbs any dye released into the wash water by the dyed items and carries such dye off in the removed wash water and rinse water, so that it does not deposit on any white or light colored laundry items. This action of the bentonite is specific to essentially nonionic synthetic organic detergent compositions and to wash waters that contain only (or essentially only) the present nonionic detergent component, present in sufficient anti-deposition proportion. In some instances a low molecular weight polyvinyl pyrrolidone may be present in the detergent compositions to reduce dye transfer further. Various other usual detergent composition builders, functional components, adjuvants and fillers may be present in the invented compositions, together with some water, provided that they are non-interfering. Bleaching compounds and optical brighteners are best omitted or essentially omitted, to improve dye stability of the dyes of the colored laundry items (although comparatively small proportions thereof may be acceptable).

This application relates to heavy duty laundry detergent compositions. More particularly, it relates to such compositions, and to wash waters in which they or their components are present, that contain a nonionic detergent as the principal deterative component, a builder for the nonionic detergent and a scavenging clay, such as bentonite, which sorbs any dye released into the wash water from colored laundry and, due to the presence of the nonionic detergent in such wash water, prevents such sorbed dye from coloring any white or lighter colored laundry items that may be present in the wash water. Also within the invention are processes for manufacturing the described compositions and for using them and components thereof to wash mixed colored and light or uncolored laundry, without dye transfer between laundry items.

Dye transfer from darker colored laundry items to lighter colored or white items during washing of mixed laundry in washing machines has long been recognized as a serious problem by manufacturers and marketers of laundry detergent compositions and consequently, preventing or minimizing such transfers has been the subject of research in the laboratories of such manufacturers. One solution to the problem was described in European Patent Specification No. 0 372 291 A1, wherein reduced dye transfer was obtained when the detergent composition employed was a mixture of anionic and nonionic detergents with a water soluble polymer, which polymer acted in such compositions as a dyeing inhibitor. Among the suitable polymers mentioned in the European specification are those of N-vinyl pyrrolidone. In another European patent specification, No. 0 299 575 A1, there is disclosed the use of polymeric clay flocculating agents, such as long chain polymers and copolymers, with smectite-type clays to increase softening effects of such clays on laundry during washing thereof. Among a list of monomers from which such agents may be made, vinyl pyrrolidone is mentioned. This teaching would lead one to believe that polyvinyl pyrrolidone (PVP) would promote deposition of such smectite clays on laundry, which is the opposite of the effect that has been observed when the compositions of the present invention are employed in the washing of laundry items, especially when the compositions are low in phosphate content and the dye-receptor fabric is of cotton.

Applicants are aware of a patent granted to their co-researchers in the laboratories of their assignee company which disclose fabric softening compositions, including detergent compositions, that include nonionic detergent or emulsifier with bentonite and a pentaerythritol compound (PEC), such as pentaerythritol distearate. Such patent is No. 5,126,060. which requires the presence of the PEC, which acts to improve the deposition of the bentonite and to increase fabric softening thereby. PEC is not a required component of the present compositions and the bentonite of such compositions does not deposit on and soften the washed laundry.

Built synthetic organic detergent compositions have been on the market for a long time (over fifty years) and the builders employed in them, such as sodium tripolyphosphate, significantly increase their power to clean soiled laundry items. Although most built synthetic organic detergent products marketed have been based on anionic detergents, nonionic detergent-based products have been marketed successfully, too. Some commercial products contain smectite clays, such as bentonite, for their fabric softening action (due to the clay being held to the fabric of the item being washed, and acting on it as a lubricant, somewhat in the manner of graphite). Most such products depend on the presence of anionic detergent to promote adherence of the clay to the fabric.

Despite the uses of the nonionic detergent, bentonite and builder separately and even in combinations with each other in various detergent compositions, before the present invention it was not known that the invented compositions hereof would have dye transfer inhibitory activity. That is applicants' discovery, and it is a significant one because one of the main criticisms consumers have about heavy duty or built laundry detergent compositions is that white or lighter colored items being washed in the same washing machine load with darker colored items tend to pick up the color of the darker items, which can make the offending detergent compositions significantly less competitive in the marketplace.

In accordance with the present invention a heavy duty laundry detergent composition of reduced dye transfer properties and of improved dye stability during laundering of mixed colored and white fabric laundry items, comprises 4 to 20% of nonionic detergent, 5 to 30% of clay, 20 to 80% of builder for the nonionic detergent, 0 to 3% of polyvinyl pyrrolidone (PVP), essentially no per-compound and essentially no optical brightener, with any balance of the composition being selected from the group consisting of fillers, functional adjuvants and water, and mixtures thereof. In preferred forms of the invention the compositions are particulate, certain nonionic detergents and bentonite are employed and the components of the composition are present within certain preferred ranges of percentages. The invention is also of processes of manufacturing and of using such compositions, and of employing the components of the compositions in wash waters.

The nonionic detergent of the invented compositions is preferably an ethoxylated higher alcohol, wherein "higher" means of 8 to 18 carbon atoms. More preferably, such alcohol is saturated and essentially straight chain, and is of 10 to 16 carbon atoms. Still more preferably it is of 11 to 15 carbon atoms and most preferably it is of 13 to 14 carbon atoms. By essentially straight chain it is meant that the percentage of straight chain members of the group is over 60 and preferably over 70, and the remaining isomers are only slightly branched, such as with methyl or other lower alkyl (such as ethyl and propyl) branching at the 2-carbon and sometimes

also at the 3-carbon. Preferably any such branching is at the 2-carbon and is methyl branching. The described alcohols are normally homologous mixtures, so when a range is given or a compound is named it will normally be a mixture of such compounds averaging in the range or averaging at the compound carbon content mentioned. However, pure straight chain alcohols may be employed, too, of chain lengths equal to the averages previously mentioned. Similarly, the extent of ethoxylation is an average within the range of 3 to 12, preferably 5 to 10 and more preferably 7 to 9 moles, e.g., 7 to 9 moles per mole of the alcohol (or of other reactant that can produce the same or equivalent final nonionic detergent).

In place of the mentioned nonionic detergents other such nonionic detergent(s) can be substituted, preferably only in minor part (less than half the nonionic detergent content and preferably less than 20% thereof). Of the other nonionic detergents that may be employed those are preferred which are reaction or condensation products of ethylene oxide and a suitable lipophile or lipophilic material. Among such materials are Oxo-type alcohols and C₇₋₁₀ alkyl substituted phenols, such as nonyl phenol. Other members of the class of nonionic detergents, such as higher fatty acid esters of ethylene oxide-based alcohols, may also be employed. With respect to the ethylene oxide portion of the compounds, both broad range ethoxyl distribution (BRE) and narrow range ethoxyl distribution (NRE) are useful, with the NRE compounds often being preferred. Examples of the ethoxylated alcohols that are useful include Tergitol® 24-L-60N, (a NRE) and Dobanol® 25 7EO (a BRE). Other suitable nonionic detergents are described in the McCutcheon's Detergent and Emulsifiers Annuals, such as that for 1981.

Although the present detergent compositions are preferably ones which contain only nonionic detergent(s), to the exclusion of other types of detergents, or contain essentially no other detergents than those which are nonionic, relatively small proportions of other types of such nonnonionic detergents may be present without such compositions being outside this invention. Thus, the percentage of such non-nonionic detergents should be minor, with respect to the total detergent content, being less than 30% thereof for the total of amphoteric, ampholytic, zwitterionic, anionic and cationic detergents, preferably being less than 10%, more preferably less than 5% and most preferably 0%. It is considered that when such nonnonionic detergent content is less than 5% (or up to 5%) of the total synthetic organic detergent content the composition is "essentially free" of such anionic and other non-nonionic detergents.

When such relatively small percentages of anionic detergents are present they will usually be C₁₂₋₁₈ alcohol sulfates, C₁₂₋₁₅ linear alkyl benzene sulfonates, C₁₂₋₁₈ olefin sulfonates, C₁₃₋₁₅ paraffin sulfonates or C₁₂₋₁₈ alcohol polyethoxy sulfate of 1 to 20 ethoxy groups, or mixtures thereof, usually as sodium or other alkali metal salts. Listings of other types of detergents may be found in the McCutcheon texts mentioned previously.

The clays that scavenge the dyes released from colored laundry are either swellable or non-swellable smectite clays of the montmorillonite type and of these bentonite has been found to be an excellent component of the present detergent compositions. While it would be expected that to sorb dyes from aqueous media it would be desirable to employ a swellable bentonite, such as a sodium or potassium bentonite, it has been found that calcium bentonite and other non-swellable bentonites can also be used, providing that there is a source of sodium (or potassium or other "swelling" cation) present in the wash water, which apparently converts the bentonite to swelling type. In the present compositions the sodium of the sulfate polyphosphate, carbonate, silicate and any other sources thereof apparently suffices to convert the bentonite to suitable swelling form and makes it capable of sorbing the released dyes from the wash water (which sorption is most often considered to be adsorption).

The bentonite employed may be in powder form, having a particle size distribution that may be in the range of 44 to 125 microns, for example, or may be of other suitable size(s). Also, it may be agglomerated to desired size, such as in the range of sizes of the desired finished detergent composition particles. The bentonites employed may be those mined in the United States, such as Wyoming bentonite, which is a swellable sodium bentonite, or may be obtained from European sources, such as deposits located in Italy or Spain, which are usually calcium bentonites. The calcium bentonite may be treated before incorporation into the present compositions, as by reaction with sodium carbonate, to convert it to a swellable (or gelling) form, if desired, or may be added to the other components of the present compositions in non-swelling form. If used as calcium bentonite it will be desirable for the detergent composition to contain at least 1% and preferably 2 to 8%, of the bentonite weight of ionizable sodium, usually in the builder salt(s) present. Further descriptions of bentonites that are useful in the present invention may be found in U.S. patent applications S.N's. 07/755,965 and 07/756,030, hereby incorporated herein by reference.

When polyvinyl pyrrolidone (PVP) is present in the invented compositions it will very preferably be of a relatively low molecular weight, such as one in the range of 20,000 to 70,000, more preferably 30,000 to 50,000 and most preferably 40,000, e.g., 40,000 ± 4,000. The molecular weights given are those obtained by gel permeation chromatography or ultrafiltration through a membrane. Instead of polyvinyl pyrrolidone homopoly-

mers, copolymers of vinyl pyrrolidone and other monomers may be employed provided that they promote the reduction of dye transfer in washing in the manner of the homopolymer. Among such monomers may be mentioned acrylonitrile and maleic anhydride. Desirably, the molecular weights of any such copolymers should be in the ranges given for the homopolymer.

The builder in the present heavy duty detergent compositions, the presence of which promotes swelling of any non-swelling clay that may be present in the detergent compositions, is often preferably a water soluble polyphosphate. Although pyrophosphates may be employed, at least in part, as builders, the water soluble polyphosphates which are sodium salts are highly preferred builders and of these the tripolyphosphates, especially pentasodium tripolyphosphate, are most preferred. Such polyphosphates are preferably humidified (to avoid overheating due to hydration when mixed with water in the crutcher before spray drying). The humidification of detergent grade polyphosphates is well known, and need not be described further here. However, anhydrous or hydrated polyphosphates may also be employed.

In detergent compositions in which phosphates are not to be present, or in which their presence is to be limited, sometimes due to governmental regulations, they may be replaced by carbonates, silicates bicarbonates, borates, zeolites and other inorganic (preferred) and organic builders, in which cases it is more desirable, although not necessary, to incorporate PVP into the formula for improved inhibition of dye transfer (because the dispersing phosphate is omitted). The other builders than polyphosphate builder may include both water soluble and water insoluble builders. Of the latter class the most prominent are the zeolites, which have water softening properties, such as anhydrous or hydrated Zeolite 4A. Water soluble organic builders may include: citrates, such as sodium citrate; nitrilotriacetates, such as trisodium nitrilotriacetate; polycarboxylates; and polyacetal carboxylates. The water soluble inorganic builders, which usually are preferred, include alkali metal carbonates, alkali metal silicates, alkali metal bicarbonates and alkali metal borates, and such include also the alkali metal sesquisilicates and alkali metal sesquicarbonates. Of the alkali metal salts the sodium salts are usually much preferred. The sodium silicate is preferably one in which the ratio of $\text{Na}_2\text{O}:\text{SiO}_2$ is in the range of 1:1.6 to 1:2.4, more preferably 1:1.8 to 1:2.2 and most preferably 1:2 or about 1:2. Preferred principal builders, which will usually be 50% or more of the builder content of the compositions, will usually be a polyphosphate, such as sodium tripolyphosphate, for phosphate-containing compositions, or a zeolite, such as Zeolite A, for non-phosphate compositions, but sodium carbonate may also be employed as such principal builder in non-phosphate compositions.

In addition to the mentioned constituents of the invented detergent compositions, other components may also be present, or they may be omitted. Other builders for the nonionic detergent, fillers, functional adjuvants and water may be present. Of these the most often also present in these compositions is water, which acts to hydrate the polyphosphate and also helps to strengthen the spray dried base beads by hydrating them and helping to form continuous surfaces thereon.

The nonionic detergent acts to prevent or inhibit deposition of the bentonite (and scavenged dye) from the wash water onto surfaces of the washed laundry (including light colored or white cotton laundry on which such deposited color would be readily apparent and objectionable), so it is evident that other detergents that do not have such capability or which promote deposition, such as the anionic detergents should not be present (or if present should preferably be of limited concentration which does not result in noticeable dye transfer, e.g., less than 5 or 10% of the total detergent content, or less than 2 or 3% of the composition). However, it is highly preferred that the detergent content be all nonionic and of the type previously described, a higher linear saturated alcohol condensed with ethylene oxide, and that no anionic detergent be present in the invented compositions.

Other clays than bentonite may be present with the bentonite, such as other hydrated aluminum silicates of the kaolinite, attapulgite, montmorillonite, illite, hectorite and halloysite types but normally such clay content will be relatively minor with respect to the bentonite content, e.g., under 1/2 or 1/4 of such content. The important considerations in selecting such a clay are its scavenging properties with respect to the dyes released from the laundry and its non-deposition onto the laundry in the wash water, when the invented compositions containing it are employed.

The functional components include various materials that are intended to improve the detergent composition functionally, as distinguished from aesthetically. Representative of such materials are the anti-redeposition agents, such as carboxymethyl cellulose (CMC), preferably the sodium salt, which act to maintain in wash water suspension the various soils removed from the laundry during washing, and prevent such soils from redepositing on the laundry. CMC and other anti-redeposition agents also help to inhibit deposition of bentonite and other clays, as well as clayey soils, onto laundry fabrics, and thereby assist in reducing dye transfer to light colored or white laundry. Enzymes act as additional agents that selectively help to decompose and remove different types of soils from laundry, thus aiding in cleaning. These include: proteolytic enzymes (protease) for removing proteinaceous soils; amylolytic enzymes (amylases) for removing starchy soils; lipolytic

enzymes (lipases) for removing fatty or oily soils; and cellulolytic enzymes (cellulases) for modifying cellulosic surfaces of laundry items to promote removal of soils from such surfaces. Anti-foaming agents act to control foaming in the crutcher and in the washing machine. Among the compounds employed for this purpose are compounds of silicon, such as silicones. Such compounds are usually silicone or siloxane polymers, such as methyl silicones, including dimethyl silicones, and polysiloxanes. They are often marketed as relatively dilute solutions or suspensions in aqueous media, e.g., about 10%, and are useful in comparatively low concentrations for deaerating the aqueous slurry of inorganic builders that are to be spray dried to provide the base beads for the present compositions, and are useful at somewhat higher concentrations to control foaming or to prevent it in washing operations. Phosphoric acid esters (PAE's) are useful as anti-foaming agents to prevent excessive wash water foaming in the washing machine but they may be replaced by silicone oil or emulsion preparations. The PAE's are especially effective as anti-foaming agents in built nonionic detergent compositions. They are partial or complete esters of phosphoric acid, with the esterifying alcohol being a higher alcohol, preferably a higher saturated fatty alcohol, of 12 to 20 carbon atoms (on the average), more preferably a saturated fatty alcohol of 15 to 18 carbon atoms and most preferably of an average of 17 to 18 carbon atoms. The ester is preferably a monoester and/or a diester and more preferably is a mixture of monoester and diester, in approximately equal proportions (35 to 65% of one and 65 to 35% of the other) or in the 1:3 to 3:1 range. In PAE's the C₁₈ alcohol content will often preferably be greater than the C₁₆ alcohol content, causing the average alcohol carbon content to be in the C₁₇ to C₁₈ range, despite the presence of some lower alcohols too. Polyacrylates and other polymers may be present in the detergent compositions to help to control bead characteristics of the spray dried base beads and also may have desirable building effects.

The aesthetic adjuvants comprise perfumes and colorants, and the colorants include dyes and pigments. Although perfumes will almost always be present in the invented compositions colorants may be omitted. When they are present the nonionic detergent-clay combination will help to prevent discoloration of light or white laundry by them, too.

Although various fillers have been suggested for use in detergent compositions the only practical one for use in the present compositions is sodium sulfate, which also functions as a processing aid in making the slurry from which the base beads are spray dried. However, it should be mentioned here that it is possible to make compositions within the present invention without spray drying, in which case the normal crutcher mix components, less water (except water of hydration) may be dry mixed with dry components before application of the liquid state nonionic detergent to such mix and before perfuming.

While per-compounds, such as sodium perborate, have been included in many heavy duty built synthetic organic detergent formulations for their bleaching actions, it has been found that such bleaching materials should be omitted from the present compositions or the compositions should be essentially free of them, to limit the extent of dye removal from the laundry. It has also been found that optical brighteners, fluorescent dyes and other ultraviolet ray-to-visible light changers should be omitted from the invented detergent compositions or the compositions should be essentially free of them, for a similar reason. However, sometimes it may be preferred to include small proportions of per-compound and/or optical brightener in the invented compositions because they improve whitening of the laundry and thereby make the invented compositions more acceptable to the consumer. Also, the small proportions present in such cases, less than or up to 3% for the per-compound and less than or up to 0.1% for the optical brightener, which are the intended limits for the term "essentially free of" herein, do not significantly adversely affect the colors of the fabrics of the items being laundered. Preferably, the content of per-compound, will be less than or up to 2% and more preferably less than or up to 1% (most preferably 0%) and the corresponding contents for the optical brightener will be 0.05%, 0.02% and 0%, respectively.

The various components of the invented detergent have been described herein and various mixtures of them will have desirable effects in reducing dye transfer in washing machine laundering operations. However, for better results it is desirable that the components be employed in certain ranges of proportions. Thus, in a relatively broad scope of the invention the detergent composition comprises 4 to 20% of the nonionic detergent, 5 to 30% of clay and 20 to 80% of polyphosphate builder, with 0 to 3% of PVP as an optional component, and with any balance being selected from the group consisting of other builders for the nonionic detergent, fillers, functional components (which include non-nonionic detergents), aesthetic adjuvants and mixtures thereof.

A preferred phosphate-containing composition within the invention comprises 10 to 20% of ethoxylated alcohol nonionic detergent, 15 to 30% of bentonite, 25 to 40% of sodium tripolyphosphate, 0 to 3% of PVP, 0 to 10% of sodium silicate, 0 to 20% of sodium carbonate, 0.3 to 2% of enzyme(s), 0.1 to 1% of PAE, 0.001 to 0.05% of silicone, 0 to 30% of sodium sulfate and 3 to 15% of water. Percentages given herein for the silicone and for the related anti-foam silicone compounds are actual percentages of the active component, although the silicones are usually marketed as solutions or suspensions in aqueous media. The percentages of enzyme are given on an "as supplied" basis because enzymes are so marketed. However, the enzymatic activities are

measurable and provide a better measure of the enzymatic actions. For example, Savinase® 4T, a proteolytic enzyme obtained from Novo Industri, has an activity of 4 KNPU/g, minimum, and their Termamyl® 60T, an amylolytic enzyme, has an alpha-amylase activity of 60 KNU/g, minimum, and the ranges of enzyme contents may be restated accordingly.

More preferred compositions within the invention comprise 10 to 20% of the nonionic detergent, 20 to 30% of the bentonite, 27 to 37% of the sodium tripolyphosphate, 0 to 3% of PVP, 3 to 10% of sodium silicate, 3 to 10% of sodium carbonate, 1 to 2% of enzymes, 0.3 to 0.9% of PAE mixture, 0.001 to 0.01% of silicone, 1 to 5% of sodium sulfate, 0.5 to 2% of carboxymethyl cellulose, 0.2 to 1% of perfume and 5 to 12% of water. In most preferred compositions (when they contain PVP) such percentages are, in the order given, 15, 24, 32, 1.5, 7, 6.5, 1.5, 0.6, 0.002, 2.8, 1.2, 0.4 and 7.5, respectively. In such compositions because the silicone is supplied as a 10% active material, there is also present 0.018% of carrier for it, which carrier may be mostly water. Also, it is intended that each of such percentages given may be prefaced with "about" to indicate that it is not necessary for the exact percentage to be employed to make the composition one that is "most preferred".

Instead of employing a phosphate as the primary builder, as in the foregoing formulas non-phosphate built detergent compositions may be made which may include one or more non-phosphate builders, such as water insoluble zeolite and water soluble non-phosphate(s). In such compositions the proportions of nonionic detergent, clay (bentonite), builder and PVP are also 4 to 20, 5 to 30, 20 to 80 and 0 to 3. Preferred compositions of such type include 4 to 20% of nonionic detergent (NRE or BRE), 8 to 25% of clay, 10 to 30% of zeolite 5 to 20% of sodium carbonate, 0 to 10% of sodium silicate, 0 to 7% of sodium citrate, 0.3 to 2% of enzyme(s), 0.001 to 0.05% of silicone, and 1 to 15% of water. More preferably such compositions comprise 5 to 15% of ethoxylated alcohol nonionic detergent (NRE or BRE) wherein the alcohol is linear and of 12 to 15 carbon atoms and is ethoxylated with 5 to 9 moles of ethylene oxide per mole, 15 to 25% of zeolite A, 7 to 13% of sodium carbonate, 0 to 5% of sodium silicate, 1 to 5% of sodium citrate, 0.3 to 1% of proteolytic enzyme, 0.01 to 0.05% of dimethyl silicone, 0.3 to 3% of sodium carboxymethyl cellulose, 0.5 to 3% of a copolymer of acrylic acid and maleic anhydride of a molecular weight in the range of 30,000 to 100,000, 0.2 to 1% of poly phosphonate chelating agent, 0 to 30% of sodium sulfate and 5 to 10% of water. In such compositions the proportions of sodium sulfate and water may be varied and can be outside the ranges given without detrimentally affecting the compositions, so long as the product is flowable and aesthetically acceptable.

To make the invented compositions it is preferred to spray dry the non-carbonate inorganic builders from an aqueous crutcher mix, mix them with other particulate or powdered components, including carbonate, bicarbonate and/or sesquicarbonate, if present, in a tumbling drum mixer and spray or drip liquid state nonionic detergent into the tumbling mix, followed by application of perfume to the resulting product, preferably also by spraying. This results in a desired well mixed particulate product which may be characterized as homogeneous. Alternatively, up to 2% (composition basis) of the nonionic detergent may be included in the crutcher mix/(without causing tower pluming).

The crutcher mix has a solids content in the range of 40 to 60%, the balance being water, and is sprayed through nozzles (Type 5/5) into a concurrent spray drying tower in which the inlet air temperature is in the range of 200 to 400°C, preferably 200 to 300°C, and the outlet temperature is in the range of 70 to 100°C. The crutcher mix will be pumpable, and for crutcher mixes including sodium tripolyphosphate as the principal builder, solids contents in the lower part of the 40 to 60% range, e.g., 40%, will be practicable, whereas for non-phosphate crutcher mixes, e.g., those based on zeolite builder, solids contents in the upper part of the range, e.g., 60%, are feasible, as are lower solids contents. In either case, the spray dried beads resulting, usually containing from 10 to 20% of water, are of particle sizes in the range of 0.1 to 2 mm in diameter and are of bulk densities in the range of 0.5 to 0.8 g/cc. The base beads so made are then mixed in a tumbling drum type of mixer (although other types of mixers may also be employed) until all the dry components, including the bentonite and carbonate, are well dispersed in the base beads, and then the nonionic detergent, in liquid state and at a temperature in the range of 25 to 60°C, is sprayed or dripped onto the moving mix. The nonionic detergent serves to help bind the mix components together, especially upon solidification at a lower temperature, and some of it permeates the particles of product and helps to disperse such particles in the wash water, in such capacity helping the bentonite and the polyphosphate, when present, to act as dispersants, too. Perfume is then applied to the composition at a temperature that is preferably room temperature or thereabout (20 to 30°C) but which is no higher than 40°C. The final particulate product is of particle sizes in the 0.1 to 2 mm diameter range and of a bulk density in the range of 0.6 to 0.8 g/cc.

Although the particulate form of the composition is highly preferred, the invented compositions may also be in other forms and may be made in different manners. For example, liquid compositions may be made, as may be gels, usually with the various components being in the same proportions as in the particulate compositions and with the water contents thereof being in the range of 12 to 75%, with co-solvents, such as ethanol

and isopropanol sometimes being present, too, replacing some of the water, e.g., 1/10 to 1/2 thereof. The particulate or powdered compositions may also be made without spray drying of the base beads, by mixing in the polyphosphate or zeolite, silicate (in powder or solution form), sulfate and silicone (which can be omitted) with the clay and other powders, etc., in the dry mixer before application of the nonionic detergent thereto.

5 In use, the invented particulate compositions are employed in the same general manner as other detergent powders, with some variations in the procedure to minimize dye transfer and fading. The concentration of the composition in the wash water will be in the range of 0.05 to 1.5%, preferably 0.1 to 1%, more preferably 0.2 to 0.5%, and most preferably 0.3 to 0.4%, e.g., 0.35%, and the wash water temperature will usually be in the range of 10 to 95°C, preferably 10 to 60°C, more preferably 30 to 45°C and most preferably 40°C or about 40°C. 10 Washing machines utilized will very preferably be of the horizontal tumbler type, with a side opening door. The nonionic detergent formula is particularly suited to this type of washing because it does not generate as much foam as do anionic detergent formulas. The washing cycle will last from 30 to 120 minutes, including rinsings, and the cycle will normally include at least three rinsings (to remove all the clay with sorbed dye on it) after pumping out of the wash water, and thereby dye transfer to the washed light colored laundry will be prevented. 15 When the form of the detergent composition is different from particulate or powdered, such as liquid or gel, or of the various components, separately or in sub-combinations, the charge thereof to the wash water in the washing machine will be such as to make the wash water of equivalent concentrations of the various components, compared to the particulate product's charge thereof. When the various components of the composition are charged separately to the wash water the amounts thereof charged will preferably be in the following ranges: 20 0.018 to 0.065% of nonionic detergent; 0.015 to 0.1% of clay, 0.065 to 0.22% of builder and 0 to 0.019% of PVP, with the preferred ranges of concentrations of the other components that may be present being similarly proportional to their percentages in the particulate products, e.g., 0.001 to 0.01% of CMC.

The detergent compositions of this invention effectively wash soiled laundry when employed in washing machine washings of such laundry in the concentrations described, and inhibit dye transfer better than commercial products on the market that are touted as not causing dye transfers between dark colored laundry items and light colored or white laundry items. They also are found to be mild to colored laundry items and do not cause fading of colors thereof, as may occur when other detergent compositions containing the normal proportions of perborate are employed. Yet, they wash the laundry clean and, in fact, are even superior to some commercial detergents in removing soils and stains, such as greasy and particulate soils and red wine stains, from laundry. It has been found by applicants that essential omission of optical brighteners from the detergent composition is of importance in preventing color hue change during the washing of colored laundry. Thus, the invented detergent compositions effectively wash mixed charges of colored and uncolored laundry without causing objectionable fading of the colored items and without objectionable dye transfer from the colored items to those that were uncolored or lightly colored. The color purging action of the present compositions appears 35 to be a rather complex physical phenomenon in which the bentonite adsorbs any dye released from colored laundry and carries it out of the washing machine tub with the wash and rinse waters. In wash waters made from the invented compositions the bentonite does not exert any fabric softening effects, indicating that it and the adsorbed dye are not deposited on and retained by the washed laundry. Color measurements confirm such findings.

40 The following working examples illustrate but do not limit this invention. Unless otherwise indicated all parts and percentages in this specification, including the claims and the working examples, are by weight and all temperatures are in °C.

EXAMPLE 1

5

	<u>Component</u>	<u>Percent (by weight)</u>
	* Pentasodium tripolyphosphate	32.0
10	Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2$, anhydrous basis)	7.0
	Sodium sulfate, anhydrous	2.8
	Dimethyl polysiloxane (silicone)	0.002
15	Sodium carbonate, anhydrous	6.5
	Proteolytic enzyme (Savinase [®] 4T, from Novo Industri, 4 KNPu/g, minimum)	0.9
20	Amylolytic enzyme (Termamyl [®] 60T, from Novo Industri, 60 KNU/g, minimum)	0.6
	Sodium carboxymethyl cellulose	1.2
25	** Phosphoric acid ester	0.6
	*** Clay	24.0
	**** Nonionic detergent (Dobanol [®] 25 7EO)	15.0
	Perfume	0.4
30	Water	9.0
		100.0
	* Anhydrous basis	
35	** Mixture of equal parts of monoester and diester of saturated fatty alcohol of an average of 17 carbon atoms (from mixed C_{18} , C_{16} , C_{14} , and C_{12} alcohols [ratio of mono-:di-ester is in the 35:65 to 40 65:35 range])	
	*** Calcium bentonite	
	**** Condensation product of C_{12-15} essentially linear alcohol with an 45 average of 7 moles of ethylene oxide per mole	

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A particulate heavy duty built nonionic detergent composition of the above formula is made by spray drying a 47% solids content crutcher mix of the tripolyphosphate, silicate (as a 40% aqueous solution), sulfate and silicone through three type 5/5 nozzles into a concurrent spray drying tower, in which the inlet drying air temperature is in the range of 200 to 275°C and the outlet air temperature is in the range of 76 to 95°C. The crutcher mix is satisfactorily deaerated, due at least in part to the presence therein of the silicone. The spray dried beads resulting are of a moisture content of 16% $\pm$ 2%, of particle sizes in the range of 0.1 to 2 mm in diameter, and of a bulk density in the range of 0.5 to 0.8 g/cc. The beads are of rounded shapes and satisfactory strength, so as to be able to resist breakage during mixing operations. The spray dried beads are then mixed with the

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sodium carbonate, enzymes, CMC, PAE and bentonite in a rotary drum mixer and after thorough mixing of the added components with the base beads there is sprayed onto the moving surfaces of the mix the liquid state nonionic detergent, at a temperature of about 55°C (its flow temperature being about 30°C). Mixing is continued until the nonionic detergent is thoroughly distributed throughout the mix, during which mixing the nonionic detergent is partially absorbed into the base beads and powdered components and also acts as a binder to hold the various powdered components together so that they are of sizes in the desired 0.1 to 2 mm range. Perfume, also in liquid state, and at room temperature, is then sprayed or dripped onto moving surfaces of the mix (which contains the nonionic detergent), which mix is at room temperature (about 25°C) and after it is mixed in thoroughly the finished product is removed from the mixer. It is of a bulk density of about 0.7 g/cc and of particle sizes substantially all in the range of No's 20 to 100 sieves, U.S. Sieve Series (which have openings micrometres to micrometres across) (through 20, on 100).

The heavy duty laundry detergent composition made is then tested for detergency, dye transfer properties and fading effects by standardized testing procedures. For evaluation of detergency it is tested in an automatic washing machine of the horizontal drum, side door type, against a variety of standard soils on a variety of test fabrics, including cottons and synthetics, as well as blends thereof, and is found to be equal to or better than a commercial detergent composition, being especially effective against mixed greasy/particulate soils and red wine stains.

Dye transfer characteristics are measured by testing against a control, which is a commercial product that is marketed as one which allows washing of colored and white goods together without objectionable dye transfer from the colored items to the white ones. Such "control" has been analyzed and has been found to include 9% of linear alkylbenzene sulfonate, 2% of lauryl ethoxylate sulfate, 5% of nonionic detergent, 32% of zeolite, 21% of sodium citrate (as the dihydrate) and the balance of adjuvants, filler and water. In the tests blue and fuchsia colored cotton towels are washed with white cotton towels in side loading washing machines in wash waters containing 0.33% of the detergent composition of this example at 40°C over a 90 minute period, and after washing rinsing (3 times) and drying of the towels the white towels are evaluated against towels that are washed under the same conditions, using the commercial control previously described. Evaluations are by reflectometer measurements and by a human panel, and they prove that there is a significant difference in dye transfers to the white towels from the colored towels, depending on which detergent composition is used, with the experimental transferring significantly less color to the white towels than does the control. Also, the dye transfer from the colored towels to the white (or undyed) towels is not considered to be objectionable when the towels are washed with a detergent composition of the invented formula.

When the cotton towels are replaced by cotton/polyester blend cloths or all polyester fabrics in these experiments essentially the same types of results are obtained, and such results are also obtained when the colored items are dyed with dyes of other colors, including brown, purple, green and red dyes.

When polyvinyl pyrrolidone is incorporated in the invented composition, with 1.5% and 3.0% thereof of a molecular weight of about 40,000 $\pm$ 4,000 being present, replacing proportional parts of the other components, little dye transfer also results but the effect of the PVP is greater in detergent composition formulas that do not contain polyphosphate builder. Such good results are obtained whether the PVP is added in the crutcher or in the drum mixer. Also, the presence of CMC in the formula helps to inhibit dye transfer in all such cases.

Color stability tests are run in essentially the same manner as the dye transfer tests except that the white towels are omitted from the wash load, being replaced by additional colored towels (or cloths), and the control is changed to a laboratory version of a commercial detergent formula that contains perborate and optical brightener. Such control formula includes 16% of applicants' nonionic detergent, 0.6% of their PAE, 3.5% of their silicate, 25% of their tripolyphosphate, 19.8% of zeolite, 1.2% of CMC, 1% of their enzymes, 20% of sodium perborate tetrahydrate, 0.4% of stilbene optical brightener, 2% of copolymer salts (Sokalan® and the balance of water and sodium sulfate (preferably 8% of water and 2.5% of the sulfate). After completion of the washings the dried cloths are evaluated comparatively for color losses and it is found, both by machine measurements and by human panel evaluations, that the experimental formula results in significantly less color fading from those cloths dyed with bleach sensitive dyes than when the formula employed is the "commercial" detergent composition. When the experimental formula contains 1.5% or 3% of PVP of the type mentioned herein the color fading is also decreased. In all the tests mentioned, including detergency and color stability tests, the same concentration of detergent composition, 0.33%, the same water temperature, 40°C, and the same other washing equipment and conditions are employed.

EXAMPLE 2

5	<u>Component</u>	<u>Percent (by weight</u>
	Sodium tripolyphosphate, anhydrous basis	32.0
	Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2$, anhydrous basis)	4.3
10	Sodium sulfate, anhydrous	15.4
	Sodium carbonate, anhydrous	6.5
	Proteolytic enzyme (Savinase 4T)	1.0
15	Sodium carboxymethyl cellulose (CMC)	1.2
	** PAE	0.6
	Calcium bentonite (white, non-activated, from Colin Stewart Minerals, Ltd., England)	20.0
20	**** Nonionic detergent	10.0
	Water	9.0
		100.0
25	** See ** at Example 1	
	**** See **** at Example 1	

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The particulate built detergent composition of this example is made in the same manner as that described in Example 1 and the product resulting, which is of the same particle size range and bulk density, is tested for detergency, dye transfer characteristics and color stability in controlled laboratory tests. It is found to be a good detergent, of less dye transfer action than the dye transfer control formula described in Example 1, and of greater color stability than the color stability control formula described in Example 1. When the PVP of Example 1 is incorporated in the formula to the extent of 1.5% and 3% (being post-added) an improvement in dye transfer inhibition is obtained and when the CMC is omitted dye transfer increases result. When the PVP is added in the crutcher little difference in dye transfer is noted, compared to when it is post-added. In the various experiments mentioned herein when the PVP is added or when the CMC is omitted, the proportions of the other components of the formula are adjusted proportionally. Alternatively, the proportion of sodium sulfate (filler) may be changed accordingly, keeping the percentages of other components the same.

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EXAMPLE 3

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	<u>Component</u>		<u>Percent (by weight)</u>
	TPP		32.0
	Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:2$)		4.3
10	Sodium sulfate		7.9
	Sodium carbonate		6.5
	Proteolytic enzyme (Savinase 4T)		1.0
15	** PAE		0.6
	+ Calcium bentonite		20.0
	**** Nonionic detergent		16.0
20	PVP (MW = 40,000 $\pm$ 4,000)		1.5
	CMC		1.2
	Water		9.0
			100.0
25	**, + and **** See descriptions in Example 2		

30 The invented detergent composition of this formula is made in the same manner as described previously for Examples 1 and 2. The PVP is added in the crutcher and no silicone is present (as in Example 2). The particulate detergent composition resulting is of particle size range and bulk density like the compositions of Examples 1 and 2 and is of good detergent properties. It does not cause objectionable color fading, by the tests described previously, and dye transfer during washing is inhibited, so that the product is unobjectionable to users thereof and is considered to be essentially non-transferring of dyes from colored to uncolored laundry.

35 In an alternative formula the NRE Tergitol 24-L-60N replaces the BRE and a very effective detergent composition of low dye transfer property results.

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EXAMPLE 4

	Component	Percent (by weight)
5	Nonionic detergent (Dobanol 25 7EO)	6.0
	Zeolite A, anhydrous	19.0
	Sodium sulfate, anhydrous	29.045
10	Dimethyl silicone (active, in 10% emulsion or solution)	0.015
	Sodium carbonate, anhydrous	10.0
	Polyphosphonate chelating compound (Dequest® 2041)	0.44
15	Sodium citrate	3.0
	Sodalan® CP5 (copolymer of acrylic acid and maleic anhydride of molecular weight of about 70,000)	1.1
20	Sodium carboxymethyl cellulose	1.0
	Proteolytic enzyme (Savinase®, mf'd. by Novo Industri)	0.4
	Calcium bentonite	23.0
25	Water (including zeolite water of hydration)	7.0
		<u>100.0</u>

This non-phosphate built detergent composition is made by essentially the same procedure as was described previously in Example 1, with the crutcher slurry including the zeolite, sulfate, polyphosphonate, silicone, sodium citrate and water, and with such mix being spray dried to a moisture content of about 11%, after which it is mixed with the remaining components except for the nonionic detergent, which is post sprayed onto the mix while in liquid state. The resulting unperfumed product, when tested in the manner previously described for detergency, dye transfer resistance and fading resistance, is found to be significantly better than a control in which the bentonite is replaced by sodium sulfate (as a filler), in dye transfer resistance. When the control includes a usual bleaching proportion of a perborate or other per-compound the experimental product is significantly better than the control in fading resistance. It is also the equivalent of the first control product in cleaning power.

Such results are obtained with the described formula when tested against dyed natural and synthetic and natural/synthetic fiber blends, such as cotton and cotton/polyester blend. Similar results are obtained when the proportion of calcium bentonite is varied over the 5 to 30% range but the dye transfer resistance is better with more bentonite in the formula. When the calcium bentonite is replaced by sodium bentonite or other alkali metal bentonite the results obtainable are essentially the same. When the nonionic detergent content is varied from 4 to 20% it acts to promote cleaning and at the same time it coacts with the bentonite to aid in the adsorption of dyes by the bentonite and the discharging of the bentonite with the wash water, instead of deposition thereof on the laundry fabric fibers. The more nonionic detergent present in the formulas the more effective it is in promoting better cleaning and better resistance to dye transfers. When up to 3% of sodium perborate or other per-compound and/or up to 0.1% of optical brightener or fluorescent dye are in the invented compositions (when such compositions are essentially free of such materials) the washed laundry appears to be cleaner and brighter and the dye transfer effects are not significantly different from those when such materials are omitted entirely.

When different nonionic detergents, builder mixes, functional components and adjuvants are employed in the invented compositions or when such functional components and adjuvants are omitted good cleaning and dye transfer inhibition are obtainable too but usually it will be preferred to have the compositions possess the additional properties conferred by such components and adjuvants. In one such formula variation the builder may include 10% of Zeolite A and 16% of sodium tripolyphosphate as the main builder combination with the sodium sulfate content being decreased to 22.045% to compensate. In products intended for the retail market perfumes will usually be present, normally up to 1 or 2% thereof, often in replacement of the sulfate filler, and

the cleaning power and dye transfer resistance will be essentially the same as for the products that do not contain perfume.

EXAMPLE 5

When the proportions of the components of the compositions described in Examples 1-3 are varied $\pm 10\%$, 20 and 30%, while still being held within the ranges mentioned in this specification, detergent compositions are obtained that are at least equivalent in detergency to controls, and do not cause objectionable dye transfers or color fadings. The compositions described are superior in dye transfer inhibiting and color stability to many commercial detergent products, even to those that have been marketed as especially good for dye transfer inhibition and color stability properties. Similarly, when the components are changed to others within the description given herein, such as other nonionic detergents of different higher alcohol chain lengths and different ethylene oxide : alcohol molar ratios, different polyphosphates, different builders, different enzymes, such as cellulase in addition to protease and amylase, and different clays, such as sodium bentonite in place of calcium bentonite, useful products within the invention and with the desirable characteristics mentioned for the invented products are obtainable. Also, liquid state products can be made by diluting the particulate compositions with water, and adding an emulsifier and/or a solvent when that is considered to be desirable. By adding water (sometimes with an organic solvent) and a gelling agent to the components of the particulate products one can make gel versions of the products.

When anionic detergents, such as sodium linear tridecylbenzene sulfonate and lauryl alcohol ethoxylate sulfate (3 EtO per mole) or mixtures thereof are completely substituted for the nonionic detergent described herein dye transfer is increased, which is objectionable, and when per-compounds and/or optical brighteners are present in the described compositions in amounts greater than the limits previously given objectionable color fading or other color change occurs. Also, when bentonite is omitted dye transfers increase. Thus, such controls are inferior to the invented products.

The particulate detergent composition formulas of the invention, as described in the working examples, all contain significant proportions of detergent and builder, with little filler (sodium sulfate), and can be characterized as concentrated detergents. Therefore, lower wash water concentrations of such products are employed (near the lower ends of the ranges previously given) than of the usual detergent compositions. For example, whereas 0.85% of one typical commercial heavy duty built detergent composition might be employed according to European practice, often 0.35% of the invented concentrated product can suffice, with even less being employed when the water hardness is low (below 100 p.p.m., as CaCO_3).

Although test washings at different temperatures within the washing temperature ranges recited herein result in good detergency, little or no fadings of colors and little or no dye transfers, in usual cases one will not wash colored laundry at temperatures in excess of 60°C , to avoid color fading. Therefore, although the invented compositions may be used to wash laundry at temperatures as high as 90°C or 95°C , as a practical matter, when colored laundry is being washed an upper limit that is 60°C or about 60°C may desirably be imposed, and more preferably it will be 45°C .

From the foregoing description and the working examples given it is considered that it has been shown that utilization of nonionic detergent in combination with bentonite clay in built detergent compositions of the types described surprisingly reduces dye transfer between colored and white laundry. This is an important discovery and makes it possible to market detergent compositions that are capable of washing mixed laundry loads without objectionably coloring the white or lighter colored items during washing thereof. Such can be accomplished without resorting to adding to the washing composition new (and usually expensive) materials designed for the purpose. Instead, readily available materials that have been used in laundry products are employed to obtain the desired improvement or technical advance in the art.

The invention has been described with respect to illustrations and embodiments thereof but is not to be considered as being limited to these because one of skill in the art, with applicants' teachings before him/her, will be able to utilize substitutes and equivalents without departing from the invention.

Claims

1. A heavy duty laundry detergent composition of reduced dye transfer properties and of improved dye stability during laundering of mixed coloured and white fabric laundry items, which comprises 4 to 20% of nonionic detergent, as the major detergent in the composition, 5 to 30% of clay, 20 to 70% of builder for the nonionic detergent, 0 to 3% of polyvinyl pyrrolidone (hereinafter PVP), and with any balance of the composition being selected from the group consisting of other builders for the nonionic detergent, fillers,

functional components, adjuvants and water, and mixtures thereof.

2. A laundry detergent composition according to claim 1 characterized in that it is in particulate form and in that the nonionic detergent is an ethoxylated higher alcohol, the clay is a montmorillonite clay and a principal builder is a polyphosphate or zeolite.
3. A particulate laundry detergent composition as claimed in claim 2 characterised in that it comprises 10 to 20% of ethoxylated higher alcohol wherein the alcohol is a saturated essentially straight chain alcohol of an average of 10 to 16 carbon atoms, ethoxylated with an average of 3 to 12 moles of ethylene oxide per mole, 15 to 30% of bentonite, 25 to 40% of sodium tripolyphosphate, 0 to 3% of PVP, 0 to 10% of sodium silicate, 0 to 20% of enzyme comprising protease, amylase or cellulase, or mixtures thereof, 0.1 to 1% of phosphoric acid ester of higher alcohol (hereinafter PAE), 0.001 to 0.05% of silicone, 0 to 30% of sodium sulphate and 3 to 15% of water.
4. A particulate laundry detergent composition as claimed in claim 3 characterised in that it comprises 10 to 20% of ethoxylated saturated essentially straight chain alcohol of an average of 11 to 15 carbon atoms ethoxylated with an average of 5 to 10 moles of ethylene oxide per mole, 20 to 30% of calcium bentonite, 27 to 30% of pentasodium tripolyphosphate, 0 to 3% of PVP of a molecular weight in the range of 20,000 to 70,000, 3 to 10% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.6 to 1:2.4, 3 to 10% of sodium carbonate, 1 to 2% of a mixture of protease and amylase in a proportion in the range of 5:1 to 1:3, 0.3 to 0.9% of phosphoric acid mono- and/or di-ester of saturated fatty alcohol of 12 to 20 carbon atoms, 0.001 to 0.01% of a silicone, which is a methyl silicone, 1 to 5% of sodium sulphate, 0.5 to 2% of carboxymethyl cellulose, 0.2 to 1% of perfume and 5 to 12% of water.
5. A particulate laundry detergent composition as claimed in claim 4 characterised in that it comprises about 15% of ethoxylated saturated essentially straight chain alcohol of an average of 13 to 14 carbon atoms ethoxylated with an average of about 7 to 9 moles of ethylene oxide per mole, about 24% of calcium bentonite, about 32% of pentasodium tripolyphosphate, 0 to about 3% of PVP of a molecular weight of an average of about 40,000, about 7% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2, about 6.5% of sodium carbonate, about 1.5% of a mixture of protease and amylase in proportion of 3 parts of protease to 2 parts of amylase, about 0.6% of mixed phosphoric acid monoester and diester of saturated fatty alcohol of an average of 17 to 18 carbon atoms, about 0.002% of a silicone, which is a dimethyl polysiloxane, about 2.8% of sodium sulphate, about 1.2% of sodium carboxymethyl cellulose, about 0.4% of perfume and about 6 to 9% of water.
6. A particulate laundry detergent composition as claimed in claim 3, 4 or 5 characterised in that the particles are comprised of spray dried beads of the sodium tripolyphosphate, sodium silicate, sodium sulphate and silicone, mixed with bentonite, sodium carbonate, enzyme and phosphoric acid ester of higher alcohol, onto which liquid state nonionic detergent had been applied.
7. A laundry detergent composition as claimed in claim 1 or claim 2 characterised in that it comprises 4 to 20% of the nonionic detergent, 8 to 25% of clay, 10 to 30% of zeolite, 5 to 20% of sodium carbonate, 0 to 10% of sodium silicate, 0 to 7% of sodium citrate, 0.3 to 2% of enzyme(s), 0.001 to 0.05% of silicone and 1 to 15% of water.
8. A laundry detergent composition as claimed in claim 7 characterised in that it comprises 5 to 15% of ethoxylated alcohol nonionic detergent wherein the alcohol is linear and of 12 to 15 carbon atoms and is ethoxylated with 5 to 9 moles of ethylene oxide per mole, 15 to 25% of zeolite A, 7 to 13% of sodium carbonate, 0 to 5% of sodium silicate, 1 to 5% of sodium citrate, 0.3 to 1% of proteolytic enzyme, 0.01 to 0.05% of dimethyl silicone, 0.3 to 3% of sodium carboxymethyl cellulose, 0.5 to 3% of a copolymer of acrylic acid and maleic anhydride of a molecular weight in the range of 30,000 to 100,000, 0.2 to 1% of polyphosphonate chelating agent, 0 to 30% of sodium sulphate and 5 to 10% of water.
9. A process for manufacture of a heavy duty laundry detergent composition as claimed in anyone of claims 1 to 8 characterized in that it comprises spray drying the builder and any other inorganic, non-carbonate and non-bicarbonate builders present in the formula from an aqueous crutcher mix to beads of particle sizes in the range of 0.1 to 2 mm, mixing said spray dried beads with an the clay and any other remaining solid state components of the formula, and spraying onto surfaces of such mixture, while it is in motion in mixing apparatus, the nonionic detergent, in liquid state, and any perfume that may be present, also

in liquid state.

- 5 10. A process as claimed in claim 9 characterized in that the heavy duty laundry detergent composition is particulate and comprises 10 to 20% of nonionic eg ethoxylated saturated essentially straight chain alcohol of an average of 11 to 15 carbon atoms ethoxylated with an average of 5 to 10 moles of ethylene oxide per mole, 20 to 30% of calcium bentonite, 27 to 37% of builder eg pentasodium tripolyphosphate, 0 to 3% of PVP eg of a molecular weight in the range of 20,000 to 70,000, 3 to 10% of sodium silicate eg of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.6 to 1:2.4, 3 to 10% of sodium carbonate, 1 to 2% of enzymes eg of a mixture of protease and amylase in the proportion in the range of 5:1 to 1:3, 0.3 to 0.9% of PAE eg phosphoric acid mono- and/or di-ester of saturated fatty alcohol of 12 to 20 carbon atoms, 0.0001 to 0.01% of a silicone, eg. which is a methyl silicone, 1 to 5% of sodium sulphate, 0.5 to 2% of carboxymethyl cellulose, 0.2 to 1% of perfume and 5 to 12% of water, and in that the spray drying is of an aqueous crutcher mix of the pentasodium tripolyphosphate, sodium silicate, sodium sulphate and silicone, and results in a strong bead, such spray drying is conducted in a vertical concurrent spray tower from a crutcher mix that is of a solids content in the range of 40 to 60%, at a drying gas inlet temperature in the range of 200 to 300°C, to particle sizes in the range of 0.1 to 2 mm in diameter, of a moisture content in the range of 10 to 20%, and of a bulk density in the range of 0.5 to 0.8 gram/cc, the mixing is of the spray dried particles with the calcium bentonite, PVP, if present, sodium carbonate, enzyme mixture, PAE and carboxymethyl cellulose, and any other remaining solid state components of the formula, and the spraying onto the surfaces of the mixture resulting is spraying of the nonionic detergent, in melted state, at a temperature in the range of 25 to 60°C onto the moving surfaces of the mixture components as they are mixed in a tumbling drum mixer, after which the perfume, in liquid state, is applied to the tumbling beads, which are at a temperature no higher than 40°C, which process results in a particulate heavy duty laundry detergent composition of particle sizes in the range of 0.1 to 2 mm in diameter and of a bulk density in the range of 0.6 to 0.8 g/cc.
- 25 11. A process of washing laundry which contains dyed and undyed fabric laundry items, which comprises washing such laundry in a washing machine in wash water containing 0.018 to 0.065% of nonionic detergent, as the only detergent in the wash water, 0.015 to 0.1% of clay, 0.065 to 0.22% of builder for the nonionic detergent and 0 to 0.019% of PVP, which wash water is essentially free of per-compound and essentially free of optical brightener, at a wash water temperature in the range of 10 to 95°C, pumping out the wash water from the washing machine, with such wash water containing the bentonite with dye removed from the dyed fabric laundry items sorbed by it, and rinsing the washed laundry of any remaining bentonite with dye sorbed by it.
- 35 12. A process of washing laundry which contains dyed and undyed fabric laundry items, which comprises washing such laundry in a washing machine characterized in that the wash water is made by admixing with water in a washing machine 0.1 to 1% of a heavy duty laundry detergent composition as claimed in anyone of claims 1 to 8 and the washing is conducted at a wash water temperature in the range of 30 to 45°C.
- 40 13. A process as claimed in claim 10 characterised in that the heavy duty laundry detergent composition comprises 6 to 20% of nonionic detergent, 5 to 30% of clay, 20 to 70% of polyphosphate builder for the nonionic detergent and 0 to 3% of PVP, and which is essentially free of per-compound and essentially free of optical brightener with any balance of such composition being selected from the group consisting of fillers, functional components, adjuvants and water, and mixtures of any two or more thereof, the washing is in a horizontal drum type washing machine, the wash water is at a temperature of about 40°C, the wash cycle, including rinsing, lasts from 30 to 120 minutes and the wash cycle includes at least three rinsings.