

"SOIL RELEASING DETERGENT"

- The present invention relates to detergent compositions which are useful for washing synthetic organic polymeric fibrous materials, such as polyesters, and which impart soil releasing properties to such washed materials. More particularly, the invention relates to such compositions in particulate form which contain as the soil releasing agent therein a copolymer of polyethylene terephthalate and polyoxyethylene terephthalate, a nonionic detergent, an alkaline builder which can decrease the soil releasing effectiveness of the soil releasing material when in contact with such material during storage, and a stabilizing proportion of polyvinyl pyrrolidone (PVP) to help to maintain the soil releasing characteristics of the soil releasing copolymer despite the presence of the alkaline builder.
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- In U.S. Patent Applications Serial Nos. 396,637 (Giordano & Ciallella) and 396,761 (Giordano & Ciallella) there were described built nonionic synthetic organic detergent compositions which contain a preferred type of soil releasing copolymer of polyethylene terephthalate and polyoxyethylene terephthalate. When polyester or polyester-cotton blend fabrics and items made from such fabrics have been washed in the described products such fabrics acquire soil releasing properties so that when they are subsequently soiled with a lipophilic material, such as dirty motor oil, such soil can more readily
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- be removed during washing of the fabric, whether such washing is with the detergent composition of that invention or with a conventional laundry detergent product. In U.S. Patent Application Serial No. 396,762 (Wixon) it is taught that the mentioned type of soil releasing polymer of polyethylene terephthalate and polyoxyethylene terephthalate can be dissolved in molten nonionic detergent and the solution can then be sprayed onto absorbent spray dried beads of builder material. The described compositions and the method for the manufacture thereof are useful but in some cases, as when the builder is alkaline, its presence can adversely affect the soil releasing capability of the soil releasing polymer in the mentioned detergent compositions, after storage at room temperatures and especially after storage at elevated temperatures. This appears to be due to the sensitivity of the soil release promoting polymer to hydrolysis. We have now discovered that when PVP, preferably of a certain type (molecular weight range), is present in the detergent composition in intimate contact with the soil releasing polymer, sometimes coating it, the soil releasing capability of the detergent composition containing such polymer is significantly improved after storage, compared to a similar product in which no PVP is present.

- In accordance with the present invention a particulate built nonionic synthetic organic detergent composition for washing synthetic organic

- polymeric fibrous materials and imparting soil release properties to them comprises a deterative proportion of a nonionic synthetic organic detergent, a building proportion of a water soluble alkaline builder for such detergent, a soil releasing proportion of a soil releasing polymer of polyethylene terephthalate and polyoxyethylene terephthalate, and a stabilizing proportion of polyvinyl pyrrolidone (PVP) for stabilizing the soil releasing polymer in the presence of the alkaline builder. Preferably, the water soluble alkaline builder salt will be sodium tripolyphosphate (normally pentasodium tri-polyphosphate), which may be accompanied by sodium silicate, a certain type of polymer of polyethylene terephthalate and polyoxyethylene terephthalate will be used, the nonionic detergent will be a condensation product of higher fatty alcohol and ethylene oxide, and the PVP will be water soluble and within a given molecular weight range. Limited proportions of moisture and adjuvants may also be present in the compositions of the present invention. Also within the scope of the present invention are processes for the manufacture of the described stabilized soil releasing detergent compositions, and methods for washing materials with such compositions.

- Although various nonionic detergents of satisfactory physical characteristics may be utilized, including condensation products of ethylene oxide and propylene oxide with each other and with hydroxyl-containing bases, such as nonyl phenol and

- Oxo-type alcohols, for best results it is highly preferred that the nonionic detergent be a condensation product of ethylene oxide and higher fatty alcohol. In such products the higher fatty alcohol
5. is of 10 to 20 carbon atoms, preferably 12 to 15 or 16 carbon atoms, and the nonionic detergent contains from about 3 to 20 or 30 ethylene oxide groups per mole, preferably from 6 to 11 or 12. Most preferably, the nonionic detergent will be one in
  10. which the higher fatty alcohol is of about 12 to 15 or 12 to 14 carbon atoms and which contains from 6 or 7 to 11 moles of ethylene oxide. Among such detergents is Alfonic (Registered Trade Mark) 1214-60C, sold by the Conoco Division of E.I. DuPont
  15. de Nemours, Inc., and Neodols (Registered Trade Mark) 23-6.5 and 25-7, available from Shell Chemical Company. Among their especially attractive properties, in addition to good detergency with respect to oily and greasy soil deposits on goods to
  20. be washed, and excellent compatibility with the present polymeric release agents, is a comparatively low melting point, which is still appreciably above room temperature, so that they may be sprayed onto base beads as a liquid which solidifies quickly
  25. after it has penetrated into the beads (m.p. usually being in 40 to 55°C range).

Various builders and combinations thereof which are effective to complement the washing action of the nonionic synthetic organic detergent(s) and to

30. improve such action include both water soluble and

water insoluble builders. Of the water soluble builders, which preferably are employed in the present invention, and are preferably in admixture, both inorganic and organic builders may be useful.

5. Among the preferred inorganic water soluble builders those that are best include: various phosphates, preferably polyphosphates, such as the tripolyphosphates and pyrophosphates, more specifically the sodium tripolyphosphates and sodium pyrophosphates,
10. e.g. pentasodium tripolyphosphate, tetrasodium pyrophosphate; sodium carbonate, preferably as soda ash; and sodium silicate; and mixtures thereof. The sodium silicate is normally of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio within the range of 1:1.6 to 1:3, preferably 1:2.0
15. to 1:2.4 or 1:2.8, e.g. 1:2.4. Of the water soluble inorganic builder salts the phosphates will usually be employed in greater proportion, with a lesser proportion of sodium silicate, the carbonate may be employed with bicarbonate and often with a lesser
20. proportion of sodium silicate, and the silicate will rarely be used alone. Instead of individual polyphosphates being utilized it will sometimes be preferred to employ mixtures of sodium pyrophosphate and sodium tripolyphosphate in proportions within
25. 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 somewhat from the components
30. charged to the crutcher.

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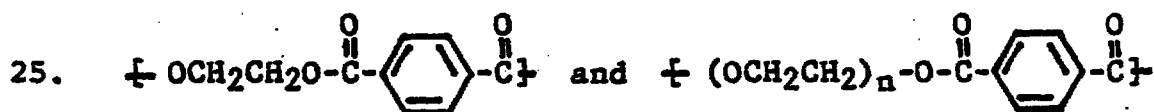
It will be noted that the water soluble builders mentioned are alkaline materials and usually the alkalinity resulting will be such that a 1% aqueous solution of the detergent composition will be of a pH in the range of about 8.5 to 12, e.g. 10.0. This alkalinity helps the detergent composition to remove various types of soil from laundry and to hold it in suspension but it also has a negative effect, tending to cause degradation of the soil releasing polymer employed and thus interfering with such polymer imparting soil releasing properties to washed materials.

Because polyesters, whether employed alone or in blends with cotton, are lipophilic, they tend to attract and hold lipophilic soils, which consequently may still be present on laundry after washing, rinsing and drying. Therefore, especially with respect to polyester fibres, the imparting of soil release properties to the fibres of materials being washed is important so that the laundering thereof may be effective. Consequently, especially because in recent years many articles of clothing and other washable household goods have been made from polyesters or polyester blends it is important that maximum soil release properties be imparted to such material. Therefore, any tendency of the soil releasing polymer being employed to degrade should be counteracted. Thus, the discovery that a certain material (PVP) stabilizes the soil releasing polymer employed in the present invention is an important one.

- The soil release promoting polymer which is an essential component of the compositions of the present invention is a polymer of polyethylene terephthalate and polyoxyethylene terephthalate which is dispersible in water and is depositable from wash water containing nonionic detergent and builder for the nonionic detergent, onto synthetic organic polymeric fibrous materials, especially polyesters and polyester blends, so as to impart soil release properties to them, while maintaining them comfortable to a wearer of clothing made from such materials and not preventing or significantly inhibiting vapour transmission through such clothing. Such polyesters have also been found to possess anti-redeposition properties and often assist in removing stains from substrates. They tend to maintain soil, especially oily or greasy soil, dispersed in wash water during washing and rinsing, so that it is not redeposited on the laundry. Useful such products are copolymers of ethylene glycol or other suitable source of ethylene oxide moiety, polyoxyethylene glycol and terephthalic acid or suitable source of the terephthalic moiety. The copolymers may also be considered to be condensation products of polyethylene terephthalate, which may sometimes be referred to as an ethylene terephthalate polymer, and polyoxyethylene terephthalate. While the terephthalic moiety is preferred as the sole dibasic acid moiety in the polymer it is within the present invention to utilize
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relatively small proportions of isophthalic acid and/or orthophthalic acid (and sometimes other dibasic acids, too) to modify the properties of the polymer. However, the proportions of such acids or sources of such supplemental moieties charged to the reaction mix, and the corresponding proportions in the final polymer will normally be less than 10% each of the total phthalic moieties present, and preferably will be less than 5% thereof.

5. The molecular weight of the polymer will be in the range of about 15,000 to 50,000, preferably being about 19,000 to 43,000, more preferably being about 19,000 to 25,000, e.g. about 22,000. Such molecular weights are weight average molecular weights, as distinguished from number average molecular weights, which, in the case of the present polymers, are often lower. In the polymers utilized the polyoxyethylene will be of a molecular weight in the range of about 1,000 to 10,000, preferably about 2,500 to 5,000, more preferably 3,000 to 4,000, e.g. about 3,400. In such polymers the molar ratio of polyethylene terephthalate to polyoxyethylene terephthalate units (considering



- as such units) will be within the range of 2:1 to 6:1, highly preferably 5:2 to 5:1, even more preferably 3:1 to 4:1, e.g. about 3:1. The proportion of ethylene oxide to phthalic moiety in the
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polymer will be at least 10:1 and often will be 20:1 or more, preferably being within the range of 20:1 to 30:1 and more preferably being about 22:1. Thus, it is seen that the polymer may be considered as

5. 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. It is considered surprising that, with such a small proportion of ethylene terephthalate or polyethylene terephthalate in the polymer, the polymer is sufficiently similar to the polymer of the polyester fibre substrate (or other polymers to which it is adherent, such as polyamides) as to be retained thereon during the washing, rinsing and drying operations. Yet, as shown by comparative experiments and various washing tests in which soil release is measured, the described polymer, in the detergent compositions of the present invention, is effective to deposit on washed synthetics, especially polyesters, so as to make them better able to be washed free of oily soil by a built nonionic detergent composition or other detergent product. It is considered that the polymer's increased hydrophilicity, attributable to the large proportion of hydrophilic ethylene oxide moieties therein, may be responsible for the excellent soil release properties which it imparts to the material upon which it is deposited, and such may also help it to coact with the built nonionic detergent.
30. Various literature articles, texts and patents

- disclose methods for the manufacture of the present polymers, included among which are Journal of Polymer Science, Vol. 3, pages 609-630 (1948); Journal of Polymer Science, Vol. 8, pages 1-22 (1951); Fibres from Synthetic Polymers, by Hill, published by Elsevier Publishing Company, New York, New York (1953), at pages 320-322; British patents 1,088,984 and 1,119,367; and U.S. Patents 3,557,039; 3,893,929; and 3,959,230. Although suitable methods
5. for making polymers useful in the present invention are described in such references it is considered that none of them discloses the particular polymers which are utilized in the present invention (but such are disclosed in the three patent applications
10. previously mentioned, and some are available commercially) and none discloses the present detergent compositions. Such polymers may be considered as having been randomly constructed from polyethylene terephthalate and polyoxyethylene terephthalate
15. moieties, such as may be obtained by reacting polyethylene terephthalate (e.g. spinning grade) and polyoxyethylene terephthalate or reacting the ethylene glycol, polyoxyethylene glycol and acid (or methyl ester) precursors thereof. Yet, it is also
20. within the invention to utilize more ordered copolymers, such as those made by reacting components of predetermined or known chain lengths or molecular weights, so as to produce what might be referred to as block copolymers or non-random copolymers. Graft
25. polymers may also be practicable.
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- The described materials are available from various sources, the products of one of which will be described in more detail here. Useful copolymers for the manufacture of the detergent compositions of this invention are marketed by Alkaril Chemicals, Inc., and commercial products of such company that we have successfully employed to produce satisfactory soil release promoting detergent compositions are those sold by them under the trademarks Alkaril QCJ and Alkaril QCF, formerly Quaker QCJ and Quaker QCF. Products available from them in limited quantities, designated by them as 2056-34B and 2056-41, have also been found to be acceptable. The QCJ product, normally supplied as an aqueous dispersion, is also available as an essentially dry solid (QCF). When it is anhydrous or low in moisture content (preferably less than 2% moisture), it looks like a light brown wax, and in it the molar ratio of ethylene oxide to phthalic moiety is about 22:1. In a 16% dispersion in water the viscosity at 100°C, is about 96 centistokes. The 2056-41 polymer is like a hard, light brown wax and in it the hydrophile:hydrophobe ratio is about 16 to 1, with the viscosity being about 265 centistokes. The 2056-34B polymer appears to be a hard brown wax, with a hydrophile:hydrophobe ratio of about 10.9:1 and its viscosity, under the same conditions as previously mentioned, is about 255 centistokes. The higher the molecular weight of the polymer the lower the hydrophile:hydrophobe molar ratio may be therein and still result in

- satisfactory soil release promotion by the detergent compositions of the present invention. The QCJ and QCF polymers have melting points (by differential thermal analysis) of about 50 to 60°C (but minor proportions of such products will remain in the solid state at temperatures up to 100°C), a carboxyl analysis of 5 to 30 equivalents/10<sup>6</sup> grams and a pH of 6 to 8 in distilled water at 5% concentration. The molecular weights (weight average) are in the range of 20,000 to 25,000 and the ethylene terephthalate:polyoxyethylene terephthalate units molar ratio is about 74:26. All three of the mentioned trademarked products are water soluble or substantially water soluble in warm or hot water (at 40 to 70°C) or at least are readily dispersible, and may be characterised as of high molecular weight, over 15,000, generally in the range of 19,000 to 43,000, often preferably 19,000 to 25,000, e.g. about 22,000. In the present application when proportions of the soil release polymer are given such are on the basis of the polymer, including any insolubles therein (which can be less active as soil release agents). Ideally, the release polymer employed will be 100% water soluble.
5. Normally, for "solution" application to materials or for solution addition to a detergent composition in wash water, the copolymers useful in the present invention may be employed in aqueous dispersion. In such dispersions a surface active agent may be present to assist in maintaining the dispersion
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uniform. Only small proportions of such surface active agent will be employed, if any. Normally, the concentration of the polymer in the aqueous medium will be about 5 to 25%, on a composition

5. basis, preferably 10 to 20%, e.g. 16%, and such is the concentration at which the above-mentioned commercial products are normally supplied when a liquid form is desired. While liquid dispersions or solvent solutions of the polymer may be employed for
10. direct additions of the polymer to the medium in which the fabrics are to be treated, when the polymer is to be incorporated in a particulate detergent composition it will be preferable for it to be in solid form, preferably as an anhydrous particulate
15. solid of a particle size like that of the other components of the detergent composition. Alternatively, it may be finely divided and powdered onto spray dried beads of the other components. In more
20. preferred methods of incorporation in a detergent composition the polymer may be dissolved in nonionic detergent and sprayed onto base beads or may be prilled with carriers and mixed with the base beads. It has been found that the polymer should not be
25. added to an aqueous crutcher mix containing anionic detergent and/or builder salt and it should not be brought into contact with water soluble builder salt in the presence of moisture, especially at an
30. elevated temperature. Accordingly, to make free flowing particulate product, normally the polymer will be essentially dry or very low in moisture

content. The use of such a product also allows for the manufacture of base beads at normal moisture content without the moisture content thereof being increased objectionably by post-spraying of an aqueous dispersion of the polymer onto the beads.

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The PVP employed has been found effective in stabilizing the described soil releasing polymers in the presence of alkaline builder, and is especially effective in the presence of sodium tripolyphosphate, which may be accompanied by sodium silicate. Such PVP usually has a molecular weight in the range of about 5,000 to 200,000, preferably 10,000 to 160,000 and most preferably about 10,000 to 50,000.

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However, in some cases PVP with a molecular weight greater than 200,000 has been found useful, although not as effective as the compounds within the ranges given. Thus, PVP with a molecular weight of about 360,000 exhibits some stabilizing effect but

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normally will be uneconomic in view of the superior results obtained with the lower molecular weight products. A preferred source of PVP is GAF

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Corporation, New York, N.Y., and the preferred commercial products of that company are marketed under the designations K-15 (M.W. = 10,000), K-30

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(M.W. = 40,000) and K-60 (M.W. = 160,000). Their K-90 product has a molecular weight of about 360,000. All the described products are water soluble and additionally, are soluble in molten nonionic detergent of the type preferably employed

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in accordance with this invention (a condensation

- product of a higher fatty alcohol with ethylene oxide). Other polylactams, such as polyvinyl oxazolidinone, may also be useful in partial replacement of the PVP. Polyacrylamide and related amides possess some stabilizing properties too, but they are inferior to PVP in this respect.
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- Various suitable adjuvants may be present in the detergent compositions of the present invention, such as enzyme powder, which helps to decompose stains and other soils so as to promote their removal, thereby coacting with the soil release aiding polymer; perfumes; fluorescent brighteners; colourants (dyes and water dispersible pigments, such as ultramarine blue); bactericides; fungicides; and flow promoting agents. Some of these materials may be added in the crutcher so that they are parts of the base beads, and some of them will be post-added. Inorganic fillers, such as sodium sulphate and sodium chloride, may be utilized but preferably the proportions thereof will be limited, one reason for this being because it has been found that sodium sulphate tends to react adversely with the present polymers. Of the enzymes, both proteolytic and amylolytic enzymes may be employed, such as those sold under the tradenames Alcalase, <sup>(R.T.M.)</sup> manufactured by Novo Industri, A/S, and Maxazyme (Registered Trade Mark), both of which are alkaline proteases (subtilisin).
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- In the detergent compositions of the present invention the proportion of synthetic organic
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- nonionic detergent preferably will be from about 5 to 30%, preferably 10 to 25% and more preferably 15 or 18 to 22%, e.g. about 20 or 21%. The total proportion of water soluble alkaline builder preferably will be from about 30 to 80%, preferably from 40 to 75%, and more preferably 45 to 70%. When the builders are sodium tripolyphosphate and sodium silicate, as is preferred, the proportions thereof are preferably about 30 to 70% and 3 to 15%, respectively, more preferably 40 to 65% and 5 to 13%, e.g. 54% and 10%. The proportion of soil release promoting polymer preferably will be from about 0.5 to 20%, preferably 1 to 10%, more preferably 1 to 5% and most preferably 2 to 5%, e.g. 3%.
5. The amount of PVP is preferably in the range 0.2 to 5% by weight e.g. 0.3 to 2% by weight. The moisture content of the product will usually be from 1 to 20%, preferably 3 to 15% and more preferably 5 to 12%, e.g. 9%. Individual adjuvants preferably constitute
10. no more than 10% of the composition, more preferably being limited to 5% and often to 2 or 3%, with the total of adjuvants desirably not exceeding 25%, preferably being limited to 15% and more preferably being held to 5 or 10% of the composition. Of
15. course, mixtures of individual components of the compositions of the present invention and of adjuvants for them may often be desirably employed, and such are intended to be included when a single type of component is mentioned. Enzyme powder, when
20. present, will usually be at a concentration in the range of 0.5 to 3%, preferably 1 to 2%. Such enzyme powder is commercially available as a mixture of active enzyme and
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carrier material, e.g. Maxazyme 375.

- The detergent compositions, whether previously manufactured and stored before use, or made immediately prior to use, may be employed in dilute aqueous solution (or dispersion) in wash water to
5. wash all-synthetic materials, including polyesters; cotton-synthetic blends, including cotton-polyester blends; cottons; nylons; and mixtures of such materials. Normally the dry weight of materials
  10. being washed will be from 2 to 15 or 20% of the weight of the aqueous washing medium, and preferably 5 to 10% thereof. The wash will be conducted with agitation over a period from 5 minutes to 1/2 hour or one hour, often from 10 to 20 minutes, and
  15. after washing the materials will be rinsed, usually with several rinses, and will be dried, as in an automatic laundry dryer. The wash water will usually be at a temperature of 10 to 95°C, preferably 15 to 60°C or 20 to 50°C, and more preferably 40 to
  20. 50°C, and the concentration of the detergent composition or the equivalent components (if separately added to the wash water) will be from 0.05 to 1%, preferably from 0.05 to 0.15%, e.g. 0.06% to 0.13%. The detergent compositions desirably have a bulk
  25. density in the range of 0.2 or 0.4 to 0.9 g/cc, preferably 0.6 to 0.9 g/cc, e.g. 0.65 g/cc and such detergents of such preferred bulk density are normally employed at a concentration of about 1/4 cup (or about 40 grams) per wash, with the wash tub
  30. usually containing about 17 gallons (U.S. (64 litres)

of water for top loading machines and about 7 to 8 gallons (26 to 30 litres) for front loaders.

When a "European" type of washing machine is employed, wherein higher concentrations of detergent

5. composition are utilized, with lesser amounts of water, and which machines usually operate at higher washing temperatures, it may be preferable to lower the washing temperature for best deposition of the polymer on the washed materials. The upper portion
10. of the broad range of detergent composition concentrations previously given may be considered as appropriate for European washing conditions whereas the corresponding intermediate and lower parts are for "American" type front loading and top loading
15. washers and washing conditions, often with the concentration for the front loading machines being lower than that for the top loaders.

The proportions of the individual active components of the compositions of the present

20. invention in the wash water will normally be from 0.001 to 0.14% of nonionic detergent, 0.006 to 0.40% of builder, 0.0001 to 0.10% of soil releasing agent and 0.00002 to 0.5% of PVP. Preferably such proportions will be from 0.003 to 0.02%, 0.02 to 0.05%,

25. 0.0003 to 0.01%, and 0.00006 to 0.006%, respectively. When sodium tripolyphosphate and sodium silicate are present in the wash water the normal percentages of the significant components of the compositions of the present invention that will be in the wash water

30. are 0.0006 to 0.040% of nonionic detergent, 0.017 to

- 0.12% of sodium tripolyphosphate, 0.002 to 0.023% of sodium silicate, 0.0008 to 0.009% of soil releasing polymer and 0.00013 to 0.004% of PVP, with more preferred ranges being 0.009 to 0.013%, 0.024 to 0.039%, 0.003 to 0.008%, 0.001 to 0.003%, and 0.0002 to 0.0012%, respectively.

- The base beads which may be employed in making the compositions of the present invention are preferably spray dried from an aqueous crutcher mix which normally will contain from about 40 to about 70 or 75% of solids, preferably 50 to 65% thereof, with the balance being water, preferably deionized water, as previously described (but city water may also be employed). The crutcher mix is preferably made by sequentially adding various components thereof in a manner which will result in the most miscible, readily pumpable and non-setting slurry for spray drying. The order of addition of the materials may be varied, depending on the circumstances, but it is most desirable when "settable" crutcher mixes are employed to add the silicate solution (if any) last, and if not last, at least after the addition of any gel- or "freeze"-preventing combination of materials or processing aids, such as citric acid and magnesium sulphate. Normally it is preferable for all or almost all of the water to be added to the crutcher first, preferably at about the processing temperature, after which the processing aids (if present) and other stable minor components, including pigment and fluorescent brightener, if

- present, are added, followed by most of the builder(s), including phosphate builder, and silicate builder. Usually during such additions each component will be mixed in thoroughly before
5. addition of the next component but methods of addition may be varied, depending on the circumstances, so as to allow co-additions when such are feasible. Sometimes component additions may be in two or more parts and sometimes different components may be pre-
10. mixed before addition, to speed the mixing process. Normally, mixing speed and power will be increased as the materials are added.

- The temperature of the aqueous medium in the crutcher will usually be about room temperature or
15. elevated, normally being in the 20 to 80°C range, preferably from 30 to 75 or 80°C, and more preferably 40 to 70 or 80°C. Heating the crutcher medium may promote solution of the water soluble salts of the mix and thereby increase miscibility but the
20. heating operation, when effected in the crutcher, can slow production rates. Temperatures higher than 80°C (and sometimes those higher than 70°C) will often be avoided because of the possibility of decomposition of one or more of possible crutcher
25. mix components, e.g. sodium bicarbonate. Also, in some cases lower crutcher temperatures increase the upper limits of crutcher solids contents, probably due to insolubilizing of normally gelling or setting components. Such problems are not usually
30. encountered when the main builder present is a polyphosphate.

Crutcher mixing times to obtain good slurries can vary widely, from as little as five minutes in small crutchers and for slurries of higher moisture contents, to as much as four hours. The mixing

5. times needed to bring all the crutcher mix components substantially homogeneously together in one medium may be as little as ten minutes but in some cases can take up to an hour, although 30 minutes is a preferable upper limit. Counting any such initial
10. admixing times, normally crutching periods will be from 15 minutes to two hours, e.g. 20 minutes to one hour, but the crutcher mix should be such as to be mobile, not gelled or set, for at least one hour, preferably for two hours, and more preferably for
15. four hours or longer after completion of the making of the mix. The present mixes are stable for at least four hours. They do not set during that time when polyphosphate is the main builder, and, when carbonate-silicate mixtures are employed, an anti-
20. setting agent, such as citric acid plus magnesium sulphate, will desirably be present to delay setting.

The crutched slurry, with the builder salt(s) and other components thereof dissolved or in particulate form and uniformly distributed therein, is

25. transferred in usual manner to a spray drying tower, which is normally located near the crutcher. The slurry is dropped from the bottom of the crutcher to a positive displacement pump, which forces it at high pressure through spray nozzles at the top of a
30. conventional spray tower (countercurrent or con-

- current) wherein the droplets of the slurry fall through a hot drying gas, usually the combustion products of fuel oil or natural gas, in which the droplets are dried to desired bead form. During
5. drying absorptive beads are made, which are especially useful to absorb liquid state heated nonionic detergent, which may be post-sprayed onto them subsequently.

- After drying, the product is screened to desired
10. size, e.g. 10 to 60 or 100, U.S. Sieve Series (which have openings 2000 to 250 or 149 microns across), and is ready for application of nonionic detergent spray thereto. Although the foregoing description is of the making of spray dried inorganic builder salt
15. base beads, and such are preferred for various reasons already mentioned, such as desirable bulk density, uniformity, flowability, strength and sorption properties, it is within the invention to employ other equivalent or nearly equivalent base
20. beads, such as those which are agglomerates, mixes, granulates, grinds, prills or chopped filaments. The nonionic detergent will usually be at an elevated temperature, such as 40 to 90°C, preferably 50 to 80°C, e.g. 55°C, to assure that it will
25. be liquid; yet, upon cooling to room temperature it will desirably be solid, often resembling a waxy solid. Even if at room temperature the nonionic detergent is slightly tacky, this characteristic does not necessarily make the final composition
30. poorly flowing because the detergent penetrates to

below the bead surface (to within the bead).

However, waxy detergents are preferred. The nonionic detergent is applied to the moving or tumbling base beads in known manner, as a spray or

5. as droplets. The enzyme preparation (herein referred to as enzyme, although it is recognized that it includes a carrier material, too), soil releasing polymer, PVP and any other powdered adjuvants may be dusted onto or mixed with the
10. builder base particles, and perfume and any other liquids to be post-added may be sprayed on at a suitable point before or after addition(s) of the powder(s).

- The nonionic detergent may be sprayed onto
15. absorbent base builder beads and the soil release promoting polymer and PVP may be post-added together, with the soil release polymer being stabilized by the PVP against the degrading action of the alkaline builder base beads. Such stabilizing effect of the
20. PVP is obtained when the release promoting polymer and the PVP are in contact, preferably when contact of the release polymer and the alkaline builder is also prevented or diminished. However, two particular ways of incorporating the nonionic detergent,
25. soil release polymer and PVP in the product are highly effective and are preferred. The more preferred method is by spray drying an aqueous crutcher mix of the alkaline builder salt to produce dried absorbent particles, dissolving the formula
30. proportions of soil releasing polymer and PVP in

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- nonionic detergent in liquid state, and spraying or otherwise effectively distributing the nonionic detergent solution of the release polymer and PVP onto the surfaces of the alkaline builder beads. In
5. carrying out such a procedure it is highly desirable that the nonionic detergent be substantially or essentially anhydrous, normally containing less than 1%, preferably less than 0.5% and more preferably less than 0.2% of moisture. It is preferred that
  10. the nonionic detergent be at a temperature in the range of 40 to 90°C, more preferably 50 to 80°C, at which the normally solid and waxy detergent will be molten and at which temperature the soil release promoting polymer and the PVP will dissolve in it
  15. (in the formula proportions). Also, the base beads will preferably be warmed and are kept in motion, as in a suitable mixer, such as a rotating longitudinal drum or tube which is inclined slightly, e.g. 5 to 10° from the horizontal. The spray droplets will
  20. preferably be of a size delivered from a typical spray gun, usually being of a diameter in the range of about 0.1 to 1 mm. The mentioned spraying and mixing can be effected in times as short as one or two minutes but normally from 5 to 10 minutes may be
  25. desirable. Surprisingly, although the spraying of the liquified nonionic detergent onto the base beads brings the soil release polymer into close contact with such beads and the alkaline builder salts of which they are composed, apparently due to the
  30. presence of the PVP the soil release promoting

polymer remains stable on storage, even at somewhat elevated temperatures. Comparisons with other soil release detergent compositions of similar formulas but without the PVP show that the experimental

5. formulas are far superior in lasting soil release promoting characteristics.

Another preferred method for making a detergent composition of the present invention includes dissolving the PVP in a liquid medium, such as

10. water, a suitable alcohol, e.g. methanol, or a suitable volatile chlorinated organic solvent, such as methylene chloride. Desirable concentrations of the PVP in the solvent will normally be within the range of 5 to 25%, with higher concentrations
15. preferred when solvent removal is more of a problem, as when water is being used. The solvent solution of PVP is then applied to the particulate soil release promoting polymer, with the rate of application being such as to apply the desired
20. formula proportion of PVP to the soil release agent. Thus, for example, when it is desired that the final detergent composition contain 3% of release polymer and 0.5% of PVP, enough PVP solution will be sprayed or otherwise applied to the surfaces of the particles
25. of the release polymer to produce an intermediate product containing about 86% of release polymer and about 14% of PVP. The particle sizes of the release polymer will preferably be within the same range as the desired sizes of the nonionic detergent-builder
30. particles of the final detergent composition but

- other sizes of particles may also be employed, although they will not be as advantageous and may separate out to some extent from the detergent-builder particles. Such detergent-builder particles
5. will be made by spraying the formula proportion of molten nonionic detergent onto the absorbent builder salt base beads in a manner like that previously described. Next, the two types of particles are blended together and the formula is ready for use.
10. The detergent composition resulting is one in which the release promoting polymer is protected by the PVP from the degrading action of the alkaline builder salt. Additionally, the presence of the non-ionic detergent on the builder salt, covering
15. substantial portions of the surfaces thereof, further helps to prevent detrimental interactions.
- In the applications of PVP to the base beads (with nonionic detergent and release polymer) and to the release polymer particles the PVP protects the
20. release polymer from the alkaline builder and furthermore, improves the product otherwise. PVP possesses useful anti-redeposition properties and has been observed to promote stain removal from laundry. In the present compositions it aids in
25. soil release, especially at room temperatures or thereabout, to an extent which is greater than that attributable to stabilization of the soil release promoting polymer. A coating of the PVP helps to protect the detergent composition against the
30. effects of atmospheric moisture. Yet, PVP is readily

soluble in the wash water, leading to quick dissolution and dispersion of the detergent components.

Although many other products have been tested, none has been found to give the very desirable effects of PVP, not even other water soluble polymeric amides.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the following examples. Unless

otherwise indicated, all parts are by weight and all temperatures are in °C.

#### EXAMPLE 1

A detergent composition having the following ingredients is provided by this example.

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | <u>Percent</u> |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| 15. Pentasodium tripolyphosphate                                                                                                                                                                                                                                                                                                                                                                                                                                   | 54.3           |
| Neodol 23-6.5 (condensation product of approximately 6.5 moles of ethylene oxide and a higher fatty alcohol averaging between 12 and 13 carbon atoms per mole)                                                                                                                                                                                                                                                                                                     | 20.7           |
| 20. Sodium silicate ( $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2.4$ )                                                                                                                                                                                                                                                                                                                                                                                                 | 9.58           |
| Moisture                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 9.05           |
| 25. Soil release promoting polymer (a copolymer of polyethylene terephthalate and polyoxyethylene terephthalate of a molecular weight of about 22,000 wherein the polyoxyethylene is of a molecular weight of about 3,400, the molar ratio of polyethylene terephthalate to polyoxyethylene terephthalate units is about 3:1 and the proportion of ethylene oxide to phthalic moiety in the polymer is about 22:1, sold by Alkaril Chemicals, Inc. as Alkaril QCF) | 3.00           |
| 30.                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                |

EXAMPLE 1 (continued)

|                                                                                            | <u>Percent</u> |
|--------------------------------------------------------------------------------------------|----------------|
| Proteolytic enzyme (Maxazyme)                                                              | 1.32           |
| 5. Fluorescent brightener (Tinopal (Registered Trade Mark) 5BM)                            | 1.26           |
| Polyvinyl pyrrolidone (GAF Corporation K-15 PVP having a molecular weight of about 10,000) | 0.50           |
| Perfume                                                                                    | 0.20           |
| 10. Dye (Blue, Mix No. 5)                                                                  | 0.05           |
| Dye (Polar Brilliant Blue)                                                                 | <u>0.04</u>    |
|                                                                                            | 100.00         |

15. The above ingredients are converted into a particulate built nonionic synthetic organic detergent composition, which is useful for washing synthetic organic polymeric fibrous materials, such as those of polyesters and polyester-cotton blends,
20. and imparting soil release properties to them, by the following method. First, base beads of the tri-polyphosphate and silicate are made by dispersing the tripolyphosphate, as a finely divided powder, in water and adding to it the formula proportion
25. (9.58%) of anhydrous silicate as a 47.5% solids solution, with the solids concentration of the crutcher mix made being about 55%. The water employed is deionized but sometimes city or tap water will be substituted, providing that its hardness is less
30. than 300 p.p.m. as calcium carbonate. Preferably, fluorescent brightener and any colourants, such as

the blue dyes, which are sufficiently crutcher stable, are added to the crutcher, too. The crutcher mix is maintained at a temperature in the range of about 60 to 70°C and mixing is continuous.

5. The mixing, including addition and dropping, which are both conducted while mixing, normally takes about 20 minutes to an hour but may be undertaken for longer periods, up to four hours or more, because the phosphate-silicate-dye-brightener dispersion-solution does not tend to set in the crutcher.

15. After sufficient mixing to obtain a substantially uniform slurry, in which the fluorescent brightener and dyes will often preferably be present, during which time some moisture may be lost by evaporation, and may be replenished, if desired, the mix is dropped from the crutcher to a pump, which pumps it at a pressure of about 21 kg/sq cm into the top of a countercurrent spray tower wherein the initial drying temperature is about 430°C and the final air temperature is about 105°C. The base beads resulting are of a bulk density of about 0.5 g/cc when cooled after manufacture, and are of particle sizes in the range of No's. 10 to 100, U.S. Sieve Series (which have openings 2000 to 149 microns across). They may be screened to such range or to a particulate product having fewer smaller particles, e.g. 10 to 60 sieve U.S. Sieve Series (which have openings 2000 to 250 microns across). The moisture content of the product is about 12.1%. The base
- 20.
- 25.
- 30.

- beads are free flowing (generally with about an 80% flow rate), non-tacky, satisfactorily porous, yet firm on the surfaces thereof and are capable of readily absorbing significant proportions of liquid nonionic detergent (and dissolved QCF and PVP) without becoming objectionably tacky.

- After cooling of the spray dried base beads they are screened so that substantially all (over 95% and often over 98%) are within the range of No's. 10 to 100 sieve, U.S. Sieve Series, and are sprayed with a solution of QCF and PVP in anhydrous nonionic detergent, in final product formula proportions. Thus, 0.5 part of the PVP and 3 parts of the QCF are dissolved in 20.7 parts of Neodol 23-6.5, which is essentially anhydrous and which is at a temperature of about 71°C and is sprayed onto tumbling base builder bead surfaces, preferably while the beads are being mixed in a tumbling drum, which may be a longitudinal drum or tube inclined to the horizontal at about 8°. The spray droplets are largely of particle sizes in the 0.1 to 1 mm range and the spraying operation will be such as to result in a throughput time in the sprayer-mixer of about 10 to 20 minutes, with the enzyme and perfume being applied in the mixer after the nonionic detergent containing PVP and QCF. The resulting detergent composition particles, when cooled, are of a bulk density of about 0.65 g/cc. The product is attractive and regular in appearance, and is free flowing and non-dusting.

- The detergent compositions described above are excellent heavy duty laundry detergents and are especially useful for washing household laundry in automatic washing machines and at the same time imparting soil release characteristics to them.
5. When employed at a temperature of about 45° to 50°C and a concentration of about 0.05 to 0.15%, e.g. 0.06%, in a 17 gallon (U.S.) (64 litres) capacity washer, in the washing of normal loads of 100% polyester and 65% polyester - 35% cotton fabrics in home laundry or commercial washing machines, whether of the top loading or front loading types, or at higher temperatures and concentrations in European type washing machines, the compositions perform satisfactorily, as would be expected from a knowledge of their components, with respect to usual washing effect characteristics, but additionally they significantly promote soil release from such materials. They are also satisfactory for washing
10. nylons, cottons, acetates and blends of fibrous materials and they promote soil release from such materials too, although not to the same great extent as with the polyesters. In tests of the washing and soil release actions of the compositions a General Electric Company top loading washing machine or a Terg-O-Tometer test washer is used, the water temperature is about 45°C and the water contains a total of about 200 p.p.m. hardness as CaCO<sub>3</sub>, of mixed calcium and magnesium ions. The washing test
15. times are all about ten to fifteen minutes and the
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- 25.
- 30.

laundry:water ratio is about 1:20, by weight. Items are rinsed twice automatically and then are dried in an automatic laundry dryer or other suitable drying means.

5. The presence of the PVP with the present soil release promoting polymer significantly stabilizes the release polymer so that with the human eye and by reflectometer readings it is evident that better soil release on washing results when a detergent composition comprising the release polymer and PVP is stored for 2 to 4 weeks at elevated temperature and is then used to treat polyesters and polyester-cotton blends, compared to the same product from which the PVP was omitted (not incorporated in the
10. nonionic detergent with QCF) but which was stored and used in the same manner. For better stabilization of the polyester soil release promoter the ratio of PVP to soil release agent should be within the range of 1:15 to 1:2 or 1:1, preferably
15. 1:10 to 1:3, e.g. 1:5 or 1:6. The soil release promoting effect is more significant on repeated launderings, usually up to five launderings of the washed materials, with the present compositions (or
20. with equivalent wash water solutions).
25. In addition to users of the present products noting the improved soil release in washing normal loads of laundry containing articles soiled with oils or greases, comparative tests wherein dirty motor oil is applied to swatches of polyester and
30. polyester-cotton blend materials after such swatches

- have been washed in either the compositions of the present invention or control compositions (which are the same as those of the invention but without PVP) show improved soil release promotion for the
5. products of the present invention when both such and the control have been stored at elevated temperatures, e.g. four weeks at 45°C before being used to wash-treat the swatches. In such tests skilled observers note the improvement in soil removal by
  10. washing with a composition of the invention or a control, respectively, after first treating and then oil soiling, and such conclusions are confirmed by reflectometer checks of the washed materials. Similar results are obtained when the polyester test
  15. materials are washed with the experimental and control detergents, are soiled with dirty motor oil, and are then washed with a commercial detergent, such as a phosphate built anionic detergent of the FAB type.
  20. When variations of the above formulas are made, changing the proportions of soil release polymer and PVP plus or minus 20% and plus or minus 50%, similar results are obtainable but with the greater proportions of PVP (and release polymer) the soil release
  25. effects are better after storage, due to improved stability of the QCF. Similarly, when such changes are made in the builder, nonionic detergent (to Neodols 25-7 and 23-3) and enzyme components, keeping the formulas within the ranges previously
  30. given, useful products result, of improved soil

- release characteristics despite storage, providing PVP is present. Also, when the PVP is changed to K-30 or K-60 excellent stabilizing of the QCF results, but with K-90 the stability is less. The
5. described results are also obtainable when other polyethylene terephthalate-polyoxyethylene terephthalate copolymers are employed especially when the molecular weights and ratios are within the preferred ranges recited in the specification.

10. EXAMPLE 2

- When the compositions of Example 1 are made by spray drying the base beads, having them absorb a spray of heated nonionic detergent (at 55°C), coating QCF particles in the 10 to 100 sieve range with PVP
15. (K-15) to produce particles still in that range, and blending the two particulate intermediate compositions, in the appropriate proportions, a stabilized soil release promoting detergent results. The PVP solution used is at a concentration of about 15% in
20. methanol, water or methylene chloride, and it is applied so as to deposit the formula proportion of PVP on the QCF. Instead of using an inclined drum mixer, a fluid bed dryer (Aeromatic Co.) is employed for the coating of the QCF particles with PVP, and
25. for evaporation of the solvent.

- Although the described coating method is useful and the products resulting are of bulk density, detergency and soil release promoting characteristics for lipophilic soils that are comparable to
30. those of the products of Example 1, and are of other

good physical characteristics like those of Example 1, it is preferred to employ the absorption method described in Example 1 because it does not require any extra equipment or any additional process steps other than a mixing tank for the dissolving of the QCF and PVP in the nonionic detergent. Also, solvent recovery means are not needed and water evaporation does not have to be effected.

EXAMPLE 3

10. Results like those given in Examples 1 and 2 are also obtainable by use of other compositions, the components of which may be separately added to the wash water at the normal washing temperatures and concentrations given. While it is preferred to
15. utilize the compositions described, containing nonionic detergent, alkaline builder salt, soil release imparting polyester and PVP or other suitable polylactam or polyamide, because the components thereof are in desired proportions and are ready to
20. use, additions of different partial mixtures of components or individual components may be made to the wash water, and excellent soil release characteristics will be acquired by the polyesters and polyester-cotton blend materials being washed (and
25. treated). Of course, when the QCF or similar soil release agent is separate from alkaline builder salt there will be little or no need to stabilize the release agent. Still, even in such cases excellent imparting of soil release characteristics is
30. obtainable, employing the same washing conditions as

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previously mentioned in Examples 1 and 2, and the PVP contributes stain removal and soil dispersion properties which further help to improve the washing characteristics of the detergent composition

5. solution.

Instead of employing particulate detergent compositions, liquids may be utilized, such as more concentrated aqueous solutions, such as those of 5 to 25 parts solids, in water or in water and

10. alcoholic solvent, and these are especially useful for pre-treating before washing any portions of clothing items that are likely to be most soiled by oily materials. Such use is to prevent subsequent hard-to-remove soiling and is particularly appropriate for shirt collars and cuffs, work gloves and

15. aprons, for example. The presence of the PVP is considered to help stabilize such liquid preparations but if they are made shortly before intended use such stabilization may not be necessary.

20. Many variations of the above formulas can be made, utilizing other nonionic detergents, other builders and builder combinations, other soil release promoting polymers and other types of PVP, such as have been described in the specification.

25. Also, the various proportions may be changed within the ranges given, and useful effects of the desired types will result. It is surprising that the present compositions are so effective and of acceptable and practical stability despite storage  
30. at elevated temperatures because PVP is extremely

- water soluble and would not be expected to "insulate" the soil release agent from atmospheric moisture, which, in the presence of water soluble alkaline salt, would be expected to cause degradation of the release agent. Also, when nonionic detergent containing dissolved release agent is deposited on base beads of alkaline builder salt it would be expected that the bringing into intimate contact of the alkaline material and the QCF (or QCJ) would promote degradation of the release agent, even in the presence of PVP. Such does not happen, as has been reported above. Yet, because of the water solubility of the nonionic detergent and its hydrophilicity it would not be expected that it would restrict contact of the alkaline builder salt and the soil release promoter. In short, the present invention, in which PVP stabilizes polyester soil release promoting material against alkaline hydrolysis and degradation is unexpected and represents an important advance in the detergent art.
- 5.
  - 10.
  - 15.
  - 20.



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CLAIMS

1. A particulate built nonionic synthetic detergent composition for washing synthetic organic polymeric fibrous materials and imparting soil release properties to them which comprises a deterative
5. proportion of a nonionic synthetic organic detergent, a building proportion of a water soluble alkaline builder for such detergent, a soil releasing proportion of a soil releasing polymer of polyethylene terephthalate and polyoxyethylene
10. terephthalate, and a stabilizing proportion of polyvinyl pyrrolidone (PVP) for stabilizing the soil releasing polymer in the presence of the alkaline builder.
15. 2. A detergent composition as claimed in Claim 1 which comprises from 5 to 30% of nonionic synthetic organic detergent or a mixture of such detergents, 30 to 80% of a water soluble alkaline
20. builder salt or a mixture of such salts, 0.5 to 20% of a soil releasing polymer or a mixture of such polymers and 0.1 to 10% of PVP.
25. 3. A detergent composition as claimed in Claim 1 or Claim 2 in which the nonionic synthetic organic detergent is a condensation product of ethylene oxide and a higher fatty alcohol of 10 to 20 carbon atoms.

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4. A detergent composition as claimed in Claim 1, 2 or 3 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 moles of ethylene oxide per mole of higher fatty alcohol.
5. A detergent composition as claimed in Claim 1, 2, 3 or 4 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 15 carbon atoms and 6 to 11 moles of ethylene oxide per mole of higher fatty alcohol.
6. A detergent composition as claimed in any one of Claims 1 to 5 in which the builder salt comprises sodium tripolyphosphate, sodium silicate, sodium pyrophosphate or sodium carbonate, or mixtures thereof.
7. A detergent composition as claimed in any one of Claims 1 to 5 in which the builder is sodium tripolyphosphate with sodium silicate of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio in the range of 1:1.6 to 1:3.
8. A detergent composition as claimed in Claim 7 in which the sodium silicate is of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio within the range of 1:2.0 to 1:2.8.
9. A detergent composition as claimed in Claim 7 or Claim 8 in which the sodium silicate is of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 1:2.4.



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10. A detergent composition as claimed in any one of Claims 1 to 9 in which the soil releasing polymer is a polymer of polyethylene terephthalate and polyoxyethylene terephthalate of a molecular weight in the range of about 15,000 to 50,000, wherein the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 1,000 to 10,000, with the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units being within the range of about 2:1 to 6:1.

11. A detergent composition as claimed in Claim 10 in which the soil releasing polymer is of a molecular weight in the range of about 19,000 to 43,000, the polyoxyethylene of the polyoxyethylene terephthalate thereof is of a molecular weight in the range of about 2,500 to 5,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units thereof is within the range of 5:2 to 5:1 and the molar ratio of ethylene oxide to phthalic moiety therein is at least 20:1.

12. A detergent composition as claimed in Claim 11 in which the soil releasing polymer is of a molecular weight in the range of 19,000 to 25,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units



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in the polymers is within the range of 3:1 to 4:1 and the molar ratio of ethylene oxide to phthalic moiety therein is from 20:1 to 30:1.

5. 13. A detergent composition as claimed in Claim 12 in which the soil releasing polymer is of a weight average molecular weight of about 22,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1 and the molar ratio of ethylene oxide to phthalic moiety therein is about 22:1.
- 10.
15. 14. A detergent composition as claimed in any one of Claims 1 to 13 in which the PVP is water soluble and of a molecular weight in the range of about 5,000 to 200,000.
20. 15. A detergent composition as claimed in Claim 14 in which the PVP is of a molecular weight in the range of about 10,000 to 160,000.
25. 16. A detergent composition as claimed in Claim 15 in which the PVP is of a molecular weight in the range of 10,000 to 50,000.
30. 17. A detergent composition as claimed in Claim 16 in which the molecular weight of the PVP is about 10,000.



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5. 18. A detergent composition as claimed in any one of Claims 1 to 17 which contains nonionic detergent, phosphate, silicate, soil releasing polymer, PVP and moisture in amounts within the ranges of 10 to 25%, 30 to 70%, 3 to 15%, 1 to 10%, 0.2 to 5% and 3 to 15%, respectively.

10. 19. A detergent composition as claimed in Claim 18 in which the contents of nonionic detergent, phosphate, silicate, soil releasing polymer, PVP and moisture are within the ranges of 15 to 22%, 40 to 65%, 5 to 13%, 2 to 5%, 0.3 to 2% and 5 to 12%, respectively.

15. 20. A detergent composition as claimed in Claim 19 in which the contents of nonionic detergent, phosphate, silicate, soil releasing polymer, PVP and moisture are about 21%, 54%, 10%, 3%, 0.5% and 9%, respectively, with the balance being adjuvants
20. including enzyme, optical brightener, colourant and perfume.

25. 21. A detergent composition as claimed in Claim 2 in which the nonionic synthetic organic detergent is a condensation product of ethylene oxide and a higher fatty alcohol of 10 to 20 carbon atoms, the builder salt is selected from the group consisting of sodium tripolyphosphate, sodium silicate, sodium pyrophosphate and sodium carbonate, and mixtures
30. thereof, the soil releasing polymer is a polymer of



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- polyethylene terephthalate and polyoxyethylene terephthalate of a molecular weight in the range of about 15,000 to 50,000, wherein the polyoxyethylene of the polyoxyethylene terephthalate is of a
5. molecular weight in the range of about 1,000 to 10,000, with the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units being within the range of about 2:1 to 6:1, and the PVP is water soluble and of a molecular weight in
10. the range of about 5,000 to 200,000.

22. A detergent composition as claimed in Claim 21 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon
15. atoms with 3 to 20 moles of ethylene oxide per mole of higher fatty alcohol, the builder is sodium tripolyphosphate with sodium silicate of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio in the range of 1:1.6 to 1:3, the soil releasing polymer is of a molecular weight in the
20. range of about 19,000 to 43,000, the polyoxyethylene of the polyoxyethylene terephthalate thereof is of a molecular weight in the range of about 2,500 to 5,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units thereof is
25. within the range of 5:2 to 5:1 and the molar ratio of ethylene oxide to phthalic moiety therein is at least 20:1, and the PVP is of a molecular weight in the range of about 10,000 to 160,000, and which composition contains moisture, and the contents of
30. such nonionic detergent, phosphate, silicate, soil



44.

releasing polymer, PVP and moisture are within the ranges of 10 to 25%, 30 to 70%, 3 to 15%, 1 to 10%, 0.2 to 5% and 3 to 15%, respectively.

5.           23. A detergent composition as claimed in Claim 22 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 15 carbon atoms and 6 to 11 moles of ethylene oxide per mole of higher fatty alcohol, the soil releasing polymer is of a molecular weight in the range of 19,000 to 25,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 3:1 to 4:1 and the molar ratio of ethylene oxide to phthalic moiety therein is from 20:1 to 30:1, the sodium silicate is of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio within the range of 1:2.0 to 1:2.8, and the PVP is of a molecular weight in the range of 10,000 to 50,000, and the contents of nonionic detergent, phosphate, silicate, soil releasing polymer, PVP and moisture are within the ranges of 15 to 22%, 40 to 65%, 5 to 13%, 2 to 5%, 0.3 to 2% and 5 to 12%, respectively.
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25.           24. A detergent composition as claimed in Claim 23 in which the soil releasing polymer is of a weight average molecular weight of about 22,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400, the molar
- 30.



45.

- ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1 and the molar ratio of ethylene oxide to phthalic moiety therein is about 22:1, the sodium silicate is of
5.  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 1:2.4, the molecular weight of the PVP is about 10,000 and the contents of such nonionic detergent, phosphate, silicate, soil releasing polymer, PVP and moisture are about 21%, 54%, 10%, 3%, 0.5% and 9%, respectively, with the
10. balance being adjuvants including enzyme, optical brightener, colourant and perfume.

25. A detergent composition as claimed in Claim 1 substantially as specifically described herein
15. with reference to the accompanying examples.

26. A process for manufacturing a particulate built nonionic synthetic organic detergent composition for washing synthetic organic polymeric
20. fibrous materials and imparting soil release properties to them, which composition includes a deterative proportion of a nonionic synthetic organic detergent, a building proportion of a water soluble alkaline builder for such detergent, a soil releasing proportion
25. of a soil releasing polymer of polyethylene terephthalate and polyoxyethylene terephthalate, and a stabilizing proportion of PVP for stabilizing the soil releasing polymer in the presence of an alkaline builder, which comprises spray drying an
30. aqueous crutcher mix of the alkaline builder to



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5. produce dried particles thereof, and applying to such spray dried builder particles the nonionic detergent in liquid state containing the soil releasing polymer and the PVP, so that the nonionic detergent, soil releasing polymer and PVP are absorbed by the spray dried builder particles.

10. 27. A process as claimed in Claim 26 in which the soil releasing polymer and PVP are dissolved in the nonionic detergent, which is essentially anhydrous, and such solution is at a temperature in the range of 40 to 90°C, and it is sprayed onto the builder salt particles.

15. 28. A process as claimed in Claim 26 or Claim 27 in which the spray dried builder particles and the composition particles are of sizes within the range of No's. 10 to 100, U.S. Sieve Series, (which have openings 2000 to 149 microns across), and are  
20. of bulk densities within the range of 0.4 to 0.9 g/cc, and the solution of soil releasing polymer and PVP in substantially anhydrous liquid state nonionic detergent is at a temperature in the range of 50 to  
25. 80°C when sprayed onto and absorbed by the builder particles and such particles are being kept in motion when such spraying is being effected.

30.. 29. A process for manufacturing a particulate built nonionic synthetic organic detergent composition for washing synthetic organic polymer fibrous



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- materials and imparting soil release properties to them, which composition includes a deterative proportion of a nonionic synthetic organic detergent, a building proportion of a water soluble alkaline builder for such detergent, a soil releasing proportion of a soil releasing polymer of polyethylene terephthalate and polyoxyethylene terephthalate, and a stabilizing proportion of PVP for stabilizing the soil releasing polymer in the presence of the
5. alkaline builder, which comprises spray drying an aqueous crutcher mix of the alkaline builder to produce dried particles thereof, applying to such spray dried builder particles the nonionic detergent in liquid state so that it is absorbed by the spray
10. dried builder particles, applying PVP in a liquid medium to particles of the soil releasing polymer and mixing such resulting particles with the builder particles containing nonionic detergent.
- 15.
20. 30. A process as claimed in Claim 29 in which the nonionic detergent is essentially anhydrous and is of a temperature in the range of 40 to 90°C, the PVP is in solution in a solvent medium when it is applied to the particles of soil releasing polymer
25. and such solvent is removed from the PVP treated soil releasing polymer before blending of such polymer with the builder particles containing absorbed nonionic detergent.

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31. A process as claimed in Claim 29 or Claim 30 in which the spray dried builder particles and the detergent composition particles are of sizes within the range of No's. 10 to 100, U.S. Sieve Series, (which have openings 2000 to 149 microns across), and are of bulk densities within the range of 0.4 to 0.9 g/cc, the nonionic detergent is at a temperature in the range of 50 to 80°C and is substantially anhydrous when it is applied in the liquid state to the spray dried builder particles, and the applications of such liquid state nonionic detergent to the builder particles and of the PVP in a solvent medium in which it is dissolved to the soil releasing polymer particles are by sprayings of such liquids onto the surfaces of such particles while the particles are being kept in motion.

32. A process as claimed in any one of Claims 26 to 31 in which the nonionic detergent is a condensation product of ethylene oxide and a higher fatty alcohol of 10 to 20 carbon atoms, the builder is a salt selected from the group consisting of sodium tripolyphosphate, sodium silicate, sodium pyrophosphate and sodium carbonate, and mixtures thereof, the soil releasing polymer is a polymer of polyethylene terephthalate and polyoxyethylene terephthalate of a molecular weight in the range of about 15,000 to 50,000, wherein the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 1,000 to



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- 10,000, with the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units being in the range of about 2:1 to 6:1, and the PVP is water soluble and of a molecular weight in the range of about 5,000 to 200,000, the proportions of nonionic detergent, builder salt, soil releasing polymer and PVP are in the ranges of about 5 to 30%, 30 to 80%, 0.5 to 20% and 0.1 or 0.5 to 10%, respectively.
5. 33. A process as claimed in any one of Claims 26 to 32 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 moles of ethylene oxide per mole of higher fatty alcohol, the builder is sodium tripolyphosphate with sodium silicate of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio in the range of 1:2.0 to 1:2.8, the soil releasing polymer is of a molecular weight in the range of about 19,000 to 43,000, the polyoxyethylene of the polyoxyethylene terephthalate thereof is of a molecular weight in the range of about 2,500 to 5,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units thereof is within the range of 5:2 to 5:1 and the molar ratio of ethylene oxide to phthalic moiety therein is at least 20:1, and the PVP is of a molecular weight in the range of about 10,000 to 160,000, and which composition contains moisture, and the contents of such nonionic detergent, phosphate, silicate, soil releasing polymer, PVP and moisture in the composition are within the ranges
- 10.
- 15.
- 20.
- 25.
- 30.



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of 10 to 25%, 30 to 70%, 3 to 15%, 1 to 10%, 0.2 to 5% and 3 to 15%, respectively.

5. 34. A process as claimed in Claim 26 substantially as specifically described herein with reference to Example 1, or 1 and 3.

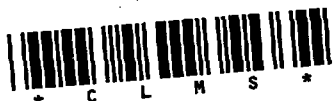
10. 35. A process as claimed in Claim 29 substantially as specifically described herein with reference to Example 2, or 2 and 3.

15. 36. A detergent composition as claimed in Claim 1 whenever made by a process as claimed in any one of Claims 26 to 35.

20. 37. A process for washing synthetic organic polymeric fibrous materials and simultaneously imparting soil release properties to them which comprises washing such a synthetic material in an aqueous medium in a washing machine tub, which medium contains a deterative proportion of a detergent composition as claimed in any one of Claims 1 to 25 or Claim 36.

25. 38. A process as claimed in Claim 37 in which the washing is of materials made of polyester or polyester-cotton blend.

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39. A process as claimed in Claim 37 or Claim 38 in which the washing temperature is in the range of 10 to 95°C.

5. 40. A process as claimed in any one of Claims 37 to 39 in which the washing temperature is in the range of 15 to 60°C and the laundry is by weight from 2 to 15% of the weight of the aqueous washing medium.

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