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(54) **Laundry additive compositions.**

(57) A laundry additive product in the form of a flexible sheet substrate in water-releasable combination with a detergent composition, wherein the composition includes a liquid processing aid selected from polyols having a molecular weight less than or equal to 180 and a boiling point of at least 100°C. Preferred polyols are glycerol, diethyleneglycol, 1,2-propane diol and 2-methyl propane-1,2-ol. The polyol provides improved resistance to product flaking when the coated substrate is exposed to abrupt changes of direction during passage through the processing equipment.

LAUNDRY ADDITIVE COMPOSITIONS

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This invention relates to the processing of laundry additive products in the form of sheet substrates coated or impregnated
5 with solidified detergent compositions, and is especially concerned with the separation of the solid impregnating and/or coating medium from the substrate during its passage through the processing equipment.

Laundry additive products in impregnated or coated sheet
10 substrate form are known in the art, being disclosed in e.g. British Patent Specification Nos. 1,586,769, 2040983 and European Published Patent Application Nos. 0013450 and 0098129. The compositions forming the coating or impregnating media for these products are primarily organic in nature and are arranged
15 to be solid at ambient temperatures whilst being releasable from the substrate by dissolution, melting, or abrasion when added to an aqueous laundry liquor. The products are also characterised by a high loading factor, i.e. a weight ratio of coating or impregnating medium to substrate of $\geq 3:1$ so that the physical
20 characteristics of the solidified coating or impregnating medium itself have to be taken into account in the handling of the coated or impregnated substrate, particularly when continuous manufacture of the product takes place.

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Continuous manufacture of a sheet substrate product of this type involves the processing of a moving web of material, and necessitates sliding and rolling contact between the coated web and portions of the equipment. Under certain conditions it has been found that separation of the coating medium from the sheet substrate can occur, particularly at points where the coated product experiences an abrupt change of direction e.g. where the moving web separates from the contact surface. This separation manifests itself as a flaky deposit on equipment and is undesirable from a number of standpoints, as it is wasteful of coating medium, is unsightly and may affect the functioning of the equipment. A need therefore exists for a processing aid which will prevent or minimise this separation from the substrate of normally solid organic coating or impregnating compositions.

The use of normally solid organic processing aids is disclosed in the above mentioned British Patent Specification Nos. 1,586,769 and 2040983 but these materials, whilst satisfactory in assisting the coating and/or impregnation of flexible sheet substrates, such as non woven textile webs, have not been found useful in preventing or minimising the flaking of product from such webs or the deposit of the separated product on processing equipment.

Surprisingly, the Applicants have now found that low levels of certain liquid polyols are useful in preventing the flaking of compositions from flexible substrates in detergent additive products of the type disclosed in the above mentioned British Patent Specifications. This reduction in flaking is particularly noticeable when coated substrate products incorporating the invention are exposed to sudden angular deflection as in folding or movement around small diameter rolls.

According to the present invention there is provided a laundry additive product comprising a normally solid detergent composition comprising a solidified liquid matrix having a melting point greater than 30°C and less than 80°C, in which matrix is dispersed solid particles of size <150 μ m

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said solid particles comprising from 5% to 50% by weight of the composition, said composition being in water releasable combination with a flexible sheet substrate, the weight ratio of said composition to said substrate lying in the range from 1:2 to 12:1 characterised in that said composition includes a liquid processing aid selected from polyols of MWt ≤ 180 and boiling point (at a pressure of 760 mm Hg) of at least 100°C in an amount of from 0.5% to 5.0% by weight of the composition.

Preferably, the liquid polyols display a solubility of less than 0.1% by weight in non polar solvents such as hexane and benzene and preferably also the liquid polyols display a high solubility in water. Most preferably the liquid polyols are completely miscible with water. The invention finds its greatest utility in those products which have a high loading factor i.e. those in which the weight ratio of the composition to the substrate is greater than 1:1, more preferably from 2:1 to 10:1, most preferably from 3:1 to 8:1.

In the context of the present invention, a material is defined as normally solid if a block of the material is self supporting at a temperature of 30°C and below. For the purposes of this invention the term 'water-releasable combination' is taken to mean a combination capable of being separated by water through solution, dispersion, leaching, softening or melting.

The laundry additive products of the present invention comprise a detergent composition of defined characteristics in water releasable combination with a flexible sheet type substrate.

The detergent compositions useful in the present invention include those exemplified in British Patent Specifications Nos. 1,586,769 and 2040983 which relate to compositions comprising an organic peroxy acid bleach precursor (so-called bleach activator) in water releasable combination with a flexible sheet substrate. Mixtures of nonionic and cationic surfactants as well as peroxy acid bleach precursors are a highly preferred components of compositions of the present invention.

In the laundry additive products of the present invention the substrate is preferably absorbent and the composition is impregnated therein. Impregnation can be carried out in any convenient manner and many methods are known in the art, such as application as a solution or dispersion from an organic solvent followed by volatilisation of the solvent. However, the preferred method is by forming a melt of those components having a melting point below 100°C, dispersing the remainder of the components in the melt, applying this melt to the substrate and cooling the impregnated substrate to provide the final product.

Coated sheet products of this type, particularly when manufactured on continuous processing equipment, are prone to suffer separation of the coating from the substrate. This separation normally manifests itself as a flaky/dusty deposit on surrounding equipment and surfaces and most frequently occurs when the coated product undergoes abrupt changes of orientation e.g. around small diameter rolls or in apparatus designed to fold the coated substrate. The severity of the problem is a function of many variables, such as the nature of the coating material, the absorbent capacity and physical form of the substrate, the weight of coating being applied and the stresses to which the coated substrate is subjected.

It has now been found that this flaky deposit can be prevented or considerably reduced by the inclusion in the detergent composition forming the coating impregnating medium of a liquid aliphatic polyol processing aid of Molecular weight ≤ 180 and boiling point $>100^\circ\text{C}$ at atmospheric pressure, in an amount of from 0.5% to 5.0% by weight of the composition, preferably from 0.5% to 3.0% by weight. Suitable polyols include glycerol and mono $\text{C}_1\text{-C}_4$ alkyl ethers and esters thereof, diethylene glycol, 1-2 propane diol and 2-methyl propane 1,2-ol. Preferred materials are glycerol and diethylene glycol.

Whilst the mechanism of the beneficial effect provided by the liquid polyols is not fully understood, it is believed that it involves a modification of the composition of the particulate solid and solidified liquid phases that result when the detergent composition is solidified after the coating and impregnation step.

The potential suitability of polyols for preventing flaking can be gauged by a screening test method which simulates the stress on coated substrates that is likely to be encountered during manufacture. The test method involves weighing the product lost and assigning a 'flaking grade' on the basis of the value obtained.

In the method a standard product is used which comprises a non woven apertured rayon sheet of basis weight 35 g/m^2 and size 350 mm x 230 mm impregnated with a composition comprising:

- 5.0g tetracetyl ethylene diamine
- 5.0g C_{14} - C_{15} primary alcohol condensed with seven moles ethylene oxide.
- 5.0g polyethylene glycol 8000
- 2.0g C_{14} alkyl trimethyl ammonium bromide.
- 0.5g ethylene diamine tetra methylene phosphonic acid.
- 0.3g maleic anhydride methyl vinyl ether copolymer (Mwt 250,000).
- 0.25g silicone suds suppressor
- 0.2g optical brightener, perfume and minors.

The Test method uses the following:

- 1 Gallenkamp shaker plus clamps
- 1 Glass lined open-ended vessel - height 400 mm, length 250 mm, width 100 mm
- 1 sheet of black card - length 250 mm, width 100 mm
- 1 digital balance accurate to 0.01g
- 1 sheet of coated/impregnated product

Procedure

- Weigh the black card accurately on the digital balance and record. Set up the tank below the clamps on the shaker and place the black card on the base of the tank. Clamp the
- 5 sheet to the shaker. Switch on the machine at its minimum setting for 1 minute, collecting all the flake falling off the sheet on the black card. Weigh the card plus flake accurately on the digital balance and record and deduct the initial card weight from the card plus flake weight.
- 10 Flaking grades are assigned on a 1-10 scale as follows, the higher numbers denoting improvement in flaking grade. Product having a flaking grade <5 is regarded as unsatisfactory.

	<u>Wt</u>	<u>Flake grade</u>
15	>0.09g	<5
	0.08 - 0.09g	5
	0.07 - 0.08g	6
	0.05 - 0.07g	7
	0.03 - 0.05g	8
20	0.01 - 0.03g	9
	<0.01g	10

On this basis various materials graded as follows:

	<u>Product</u>	<u>Additive</u>	<u>Flaking Grade</u>
	Standard product	-	5/6
25	"	0.3g/sheet sorbitol syrup	9/10
	"	0.3g/sheet sorbitol melt	8/9
	"	0.3g/sheet glycerol	9/10
30	"	0.3g/sheet diethylene glycol	9/10
	"	0.3g/sheet propylene diol	8/9
	"	0.1g/sheet glycerol	9/8
35	"	0.2g/sheet glycerol	9/9

Preferred materials are glycerol and diethylene glycol used in amounts of 0.1 - 0.3g/sheet, corresponding to a range of from 0.5% to 1.6% based on the weight of the detergent composition.

- 5 The detergent composition is normally solid i.e. can be formed into a body which is self supporting at temperatures of 30°C and below. It is composed of a solidified liquid mass, which has a melting point lying between 30°C and 80°C in which are dispersed solid particles of size $< 150 \mu\text{m}$,
10 preferably $< 50 \mu\text{m}$.

- The detergent composition comprises any of the conventional functional components normally used in laundry detergents such as surfactants of anionic, nonionic, cationic amphoteric or zwitterionic type, suds modifiers, detergent
15 builder salts, chelating agents, peroxygen bleaches, organic peroxy bleach precursors, anti-redeposition agents, antibacterial agents, fabric softening and antistatic agents, optical brighteners, anticorrosion agents, enzymes, perfumes, dyes and pigments.

- 20 Most of the above components, if present in the additive products of the invention, form the solid particulate phase which may be organic or inorganic in type or may be a mixture of the two. Certain components such as nonionic surfactants, suds modifiers and certain anti-redeposition
25 agents are solids having melting points within the temperature range required for the solidified liquid mass and so can be employed both as functional components and as carriers for the remainder.

With respect to the surfactants, those of anionic type can be natural or synthetic in origin whilst nonionic surfactants can be either semi-polar or alkylene oxide condensates. Examples of each of these classes of compounds are disclosed in Laughlin & Heuring US Patent No. 3,929,678 issued 30 December 1975. Cationic surfactants can include amine salts, quaternary nitrogen and phosphorus compounds and ternary sulphonium compounds. The invention is particularly useful in additive products incorporating a quaternary ammonium surfactant as the or part of the solid particles.

The nonionic surfactants used in the compositions may be alkoxyated aliphatic alcohols, alkyl phenols, esters, amides and fatty acids having an HLB within the range 8.0-17.0. The aliphatic alcohols include linear and branched chain primary and secondary C_8-C_{22} alcohols, the alkyl phenols are the C_6-C_{12} alkyl phenols, and the fatty esters, fatty amides and fatty acids are those having a $C_{12}-C_{18}$ alkyl group in the acyl residue. The preferred alkoxyating group is ethylene oxide.

Suitable nonionic surfactants based on aliphatic alcohols are condensation products of primary and secondary alcohols with from 4 to 30 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched and generally contains from 8 to 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol with 10 moles of ethylene oxide per mole of alcohol and the condensation product of 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms). Examples of commercially available nonionic surfactants of this type include Tergitol 15-S-9, marketed by Union Carbide Corporation, Neodol 45E9, marketed by Shell Chemical Company, and Kyro EOB, marketed by The Procter &

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Gamble Company. Other suitable alcohol ethoxylates include:-

- 5 Tallow ($C_{16}-C_{18}$) alcohol (E_{25})
 Linear ($C_{14}-C_{15}$) alcohol (E_5)
 ($C_{14}-C_{15}$) alcohol (E_7)
 ($C_{12}-C_{13}$) alcohol (E_6)
 ($C_9 -C_{11}$) alcohol (E_5)
 Branched ($C_{10}-C_{13}$) alcohol (E_4)
 Linear ($s-C_{11}-C_{15}$) alcohol (E_5)
 ($s-C_{11}-C_{15}$) alcohol (E_7)
10 ($s-C_{11}-C_{15}$) alcohol (E_9)

Alcohol ethoxylates such as those disclosed in British Patent Specification No. 1,462,134 are also useful.

15 Suitable alkyl phenol ethoxylates include the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, said ethylene oxide being present in an amount equal to 8 to 20 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for
20 example, from polymerized propylene, di-isobutylene, and the like. Examples of compounds of this type include nonyl phenol condensed with 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; and di-isooctyl phenol
25 condensed with 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630, marketed by the GAF Corporation, and Triton X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

30 Other suitable phenol ethoxylates include:-

- Linear C_8 Alkyl phenol (E_5)
 C_8 Alkyl phenol (E_8)
 C_9 Alkyl phenol (E_6)
 C_9 Alkyl phenol (E_9)

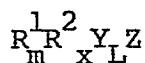
Suitable fatty acid ethoxylates include coconut fatty acid (E_5) and oleic fatty acid (E_{10}), while ester ethoxylates include:

- 5 Sorbitan monooleate (E_5)
 Sorbitan trioleate (E_{20})
 Sorbitan monostearate (E_4)
 Sorbitan tristearate (E_{20})

10 Other nonionic surfactants useful herein include the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine, and the condensation product of ethylene oxide with the product resulting from the condensation of propylene oxide with propylene glycol. Surfactants of this type are available commercially from the Wyandotte Chemicals Corporation under the names "Tetronic" and "Pluronic" respectively.

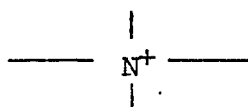
20 Particularly preferred nonionic surfactants as components of the compositions useful in the present invention are the primary linear and branched chain primary alcohol ethoxylates, such as C_{14} - C_{15} linear alcohols condensed with 7-15 moles of ethylene oxide available from Shell Oil Co. under the "Dobanol" Trade Mark and the C_{10} - C_{13} branched chain alcohol ethoxylates obtainable from Liquichimica SA under the "Lial" Trade Mark.

25 The cationic surfactants forming preferred components of the compositions useful in the present invention have the empirical formula

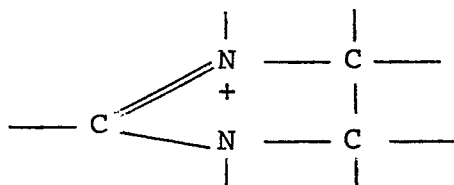


wherein each R^1 is a hydrophobic organic group containing alkyl chains, alkenyl chains, alkyl benzyl chains, alkyl phenyl chains, ether linkages, alkylene groups, alkenylene groups, ester linkages, and amide linkages totalling from 8 to 22 carbon atoms and which may additionally contain or be attached to a polyethylene oxide chain containing up to 20 ethoxy groups, m is a number from one to three provided that no more than one R^1 in a molecule can have more than 16 carbon atoms when m is 2 and no more than 12 carbon atoms when m is 3. R^2 is an alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms or a benzyl group, with no more than one R^2 in a molecule being benzyl, and x is a number from 1 to 3, Y is selected from

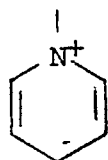
(1)



(2)



(3)



and Z is a water-soluble anion selected from halide, methosulphate, carboxylate, hydroxide, or nitrate, anion, particularly preferred being chloride, bromide or iodide anions, in a number to give electrical neutrality of the cationic component. The particular cationic component to be included in a given system depends to a large extent upon the particular nonionic component to be used in this system, and is selected such that it is at least water-dispersible, or preferably water-soluble, when mixed with said nonionic surfactant. It is preferred that the cationic component be

When used in combination with nonionic surfactants, these cationic components provide excellent soil removal characteristics, confer static control benefits to the laundered fabrics, and inhibit the transfer of dyes among the laundered fabrics in the wash solution.

$$\begin{array}{c} | \\ \text{--- N}^+ \text{---} \\ | \end{array} \quad \text{or} \quad \begin{array}{c} | \\ \text{--- C} = \text{N} \text{---} \text{C} \text{---} \\ \quad \quad \quad | \quad \quad | \\ \quad \quad \quad + \quad \quad \\ \quad \quad \quad \text{N} \text{---} \text{C} \text{---} \\ | \quad \quad | \\ \text{---} \quad \text{---} \end{array}$$

Where Y is $-N^+$ - and $m = 1$ it is preferred that x is

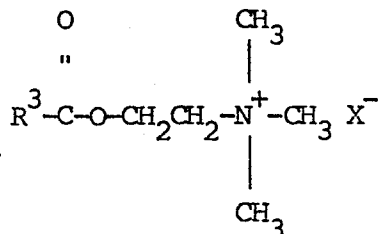
25 Where m is equal to 2, only one of the R^1 chains should be longer than 16 carbon atoms. Thus, ditallowdimethylammonium salts used conventionally as fabric softeners and static control agents in detergent compositions, are unsuitable as the cationic component in surfactant mixtures.

Preferred di-long chain cationics of this type include those in which x is equal to 2 and R² is a methyl group.

Particularly preferred cationic materials of this class include are those in which R₁ is C₈-C₁₂ alkyl such as the alkyl dimethylammonium di-C₈, salt, the di-C₁₀ alkyldimethylammonium salts and the di-C₁₂ alkyldimethylammonium salts materials.

Where m is equal to 3, only one of the R¹ chains can be greater than 12 carbon atoms in length. The reason for this chain length restriction, as is also the case with the di-long chain cationics described above, is the relative insolubility of these tri- and di-long chain materials. Where tri-long chain alkyl materials are used, it is preferred that x is equal to 1 and that R² is a methyl group. In these compositions it is preferred that R¹ is a C₈ to C₁₁ alkyl group. Particularly preferred tri-long chain cationics include trioctylmethylammonium halide, and tridecylmethylammonium halide.

Cationic components in which m is equal to 1 and the hydrophobic group R₁ is interrupted by ester linkages are disclosed in USP No. 4260529. Particularly preferred cationic surfactants of this type are the choline ester derivatives having the following formula



as well as those wherein the ester linkage in the above formula is replaced with a reverse ester, amide or reverse amide linkage.

Particularly preferred examples of this type of cationic surfactant include stearyl choline ester quaternary ammonium halide (R³ = C₁₇ alkyl), palmitoyl choline ester quaternary ammonium halides (R³ = C₁₆ alkyl), myristoyl choline ester quaternary ammonium halides (R³ = C₁₃ alkyl), lauroyl choline ester ammonium halides (R³ = C₁₁

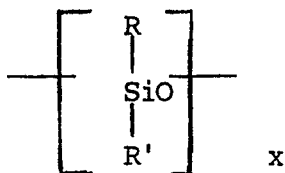
alkyl), and tallowoyl choline ester quaternary ammonium halides ($R^3 = C_{16}-C_{18}$ alkyl).

The above described cationic components are useful in nonionic/cationic surfactant mixtures which have a ratio of nonionic to cationic of from 1:2 to 20:1. Preferably, nonionic to cationic ratios of from 10:1 to 1:1 are used, more preferably from 5:1 to 3:2, most preferably from 10:3 to 10:5. These cationic surfactants may also be used in the detergent systems defined in US Patent No. 4,259,217, in nonionic to cationic ratios of from 8:1 to 20:1.

In compositions incorporating mixtures of nonionic and cationic surfactants it is preferred that the amount of the nonionic-cationic mixture is such that the surfactant mixture:substrate weight ratio lies in the range 10:1 to 1:5, preferably from 10:1 to 1:2, and most preferably from 5:1 to 1:1. In preferred executions using non-woven sheet substrates of approximately 805 cm^2 plan area and 3 grs/sheet basis weight, the loading of nonionic-cationic surfactant mixture is in the range 5-15 grs/sheet.

Suds modifiers useful in the detergent compositions can be of the suds boosting, suds stabilising or suds suppressing type. Examples of the first type include the $C_{12}-C_{18}$ fatty acid amides and alkanolamides, the second type is exemplified by the $C_{12}-C_{16}$ alkyl dilower alkyl amine oxides and the third type by $C_{20}-C_{24}$ fatty acids, certain ethylene oxide-propylene oxide copolymers such as the "Pluronic" series, silicones, silica-silicone blends, micro-crystalline waxes, triazines and mixtures of any of the foregoing.

Preferred suds suppressing additives are described in US Patent 3,933,672, issued January 20, 1976, relative to a silicone suds controlling agent. The silicone material can be represented by alkylated polysiloxane materials such as silica aerogels and xerogels and hydrophobic silicas of various types. The silicone material can be described as siloxane having the formula:



wherein x is from 20 to 2,000, and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl and phenyl. The polydimethylsiloxanes (R and R' are methyl) having a molecular weight within the range of from 200 to 200,000, and higher, are all useful as suds controlling agents. Additional suitable silicone materials which exhibit useful suds controlling properties, are those wherein the side chain groups R and R' are alkyl, aryl, or mixed alkyl and aryl hydrocarbyl groups, examples including diethyl-, dipropyl-, dibutyl-, methyl-, ethyl-, and phenylmethyl-polysiloxanes. Additional useful silicone suds controlling agents can be represented by a mixture of an alkylated siloxane, as referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m²/gm intimately admixed with dimethyl silicone fluid having a molecular weight in the range from 500 to 200,000 at a weight ratio of silicone to silanated silica of from 19:1 to 1:2. The silicone suds suppressing agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier.

Particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in US Patent No. 4,136,045. An example of such a compound is DB-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

Suds modifiers as described above are incorporated at levels of up to approximately 5%, preferably from 0.1 to 2%

by weight of the cationic-nonionic surfactant mixture.

Detergent builder salts can be inorganic or organic in type but the crystalline nature of inorganic builder salts, and hence the difficulty of incorporating them by coating or
5 impregnation puts constraints on the amounts which can be included in the products of the invention. This results in a practical upper limit on the weight ratio of inorganic builder to substrate of about 5:1. Organic builder salts such as citrates, mellitates, phytates, nitrilo triacetates,
10 carboxymethyloxy succinates, polyacrylates and polyhydroxyacrylates can be incorporated at higher levels, i.e. up to a weight ratio of builder to substrate of about 8:1.

Chelating agents that can be incorporated include citric
15 acid, nitrolotriacetic and ethylene diamine tetra acetic acids and their salts, organic phosphonate derivatives such as those disclosed in Diehl US Patent No. 3,213,030 issued 19 October, 1965; Roy US Patent No. 3,433,021 issued 14 January, 1968; Gedge US Patent No. 3,292,121 issued 9 January, 1968;
20 and Bersworth US Patent No. 2,599,807 issued 10 June, 1952, and carboxylic acid builder salts such as those disclosed in Diehl US Patent No. 3,308,067 issued 7 March, 1967.

Preferred chelating agents include nitrilotriacetic acid (NTA), nitrilotrimethylene phosphonic acid (NTMP), ethylene
25 diamine tetra methylene phosphonic acid (EDTMP) and diethylene triamine penta methylene phosphonic acid (DETPMP), and these are incorporated in amounts such that the substrate chelating agent weight ratio lies in the range 20:1 to 1:5, preferably 5:1 to 1:5 and most preferably 3:1 to 1:1.

30 Inorganic peroxygen bleaches which can be incorporated include those which are true peroxysalts such as alkali metal monopersulphates as well as salts which include hydrogen peroxide, such as sodium perborate monohydrate and tetrahydrate, sodium percarbonate, sodium persilicate and
35 sodium perpyrophosphate.

Clathrates such as that comprising $4\text{Na}_2\text{SO}_4$: $2\text{H}_2\text{O}_2$: 1 NaCl can also be incorporated provided that

moisture is excluded from the compositions. Mixing of the bleach with the other components can be employed in certain instances but where materials reactive towards the bleach such as organic peroxy acid bleach precursors are included, spatial separation of the bleach from these materials is necessary.

Organic peroxy acid bleach precursors are preferred components of laundry products of the invention and any of the precursors disclosed in British Patent Specification Nos. 1,586,769 and 2040983 British Patent Application No. 8304990 and European Published Application No. 0098129 can be included. Preferred precursors include tetra acetyl alkylene diamine, in which the alkylene group can contain from 1 to 6 carbon atoms tetra acetyl glycouril, sodium p-C₁-C₉ acyloxybenzene sulphonates in which the alkyl portion of the acyl group may be linear or branched penta acetyl glucose, octa acetyl lactose and mixtures of any of these.

Certain polybasic acids have been found to enhance the bleaching effect of organic peroxyacids, examples being EDTMP, NTMP and DETPMP. However, not all chelating polybasic acids are useful in this respect, while certain poorly-chelating polybasic acids, notably succinic acid, and glutaric acid, do show efficacy.

The level of usage of the precursor will naturally be dependent on a number of factors e.g. the size of the fabric load in the machine, the level of bleaching performance desired, the amount of perhydroxyl ion in the wash solution, the bleaching efficacy of the organic peroxy species derived from the precursor and the efficiency of conversion of the precursor into that peroxy species. It is conventional with inorganic peroxy bleaches to provide a level of available oxygen in solution from 50 ppm to 350 ppm by weight for heavy duty laundry purposes. However, when using organic peroxy bleaches a level of available oxygen provided by the organic peroxy compound may lie in the range from 2 ppm to 100 ppm, levels of from 3 ppm to 30 ppm being appropriate under conventional US washing conditions while levels of from 20 ppm to 50 ppm are more commonly used under European washing conditions. This level of available oxygen should be

attained within the normal wash cycle time i.e. within 5-25 minutes depending on the particular wash cycle being employed.

For a machine having a liquid capacity in use of 20 to 30 litres, such a level of available oxygen requires the
5 delivery of from 1 gr to 20 gr of organic peroxy compound precursor assuming quantitative conversion. Preferably a single unit of substrate should be capable of accommodating the desired level of precursor and any adjuvants and additives that it is necessary to incorporate into the
10 product, although the number of units to be used to deliver a given quantity of precursor is a matter of choice. Normally the weight of precursor per delivery will lie in the range 3 to 10 grs, preferably from 4 to 6 grs.

Anti redeposition and soil suspension agents also
15 constitute preferred components of the additive compositions of the invention. Cellulose derivatives such as methyl cellulose, carboxymethyl cellulose and hydroxy ethyl cellulose are examples of soil suspension agents and suitable antiredeposition agents are provided by homo- or co-polymeric
20 polycarboxylic acids or their salts in which at least two carboxyl radicals are present separated by not more than two carbon atoms. Polyethylene glycols of Mwt 1,000 - 10,000 particularly of Mwt 4,000 - 10,000 are also useful
pareticulate soil suspension agents and function as such even
25 if included primarily as processing aids.

Highly preferred polymeric polycarboxylic acids are copolymers of maleic acid or maleic anhydride with methyl vinyl ether, ethyl vinyl ether or acrylic acid, the polymers having a molecular weight in the range from 12,000 to
30 1,500,000.

A further description of suitable polymeric polycarboxylic acids is provided in the Applicants' European Patent Application No. 82301776.9. Levels of incorporation of these antiredeposition agents are such as to provide
35 agent:substrate ratios of 2:1 to 1:20, preferably 1:2 to 1:10.

Suitable antibacterial agents are quaternary ammonium compounds such as cetyl pyridinium chloride, cetyl trimethyl ammonium bromide and C_8-C_{18} alkyl benzyl dimethyl ammonium chloride, typically incorporated in weight ratios of agent to substrate of from 1:1 to 1:10.

A wide range of fabric softeners and antistatic agents can be included as optional compounds. Exemplary cationic nitrogen compounds include the di- $C_{16}-C_{18}$ alkyl, di- C_1-C_4 alkyl quaternary ammonium salts, imidazolinium salts and non-nitrogenous materials such as the sorbitan esters of $C_{16}-C_{18}$ fatty acids. These are normally incorporated at softener to substrate weight ratios of 5:1 to 1:1.

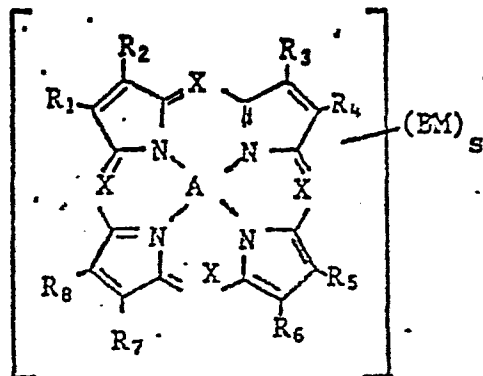
Optical brighteners may be anionic or nonionic in type and are added at levels of from 0.05 to 1.0 grs per sheet preferably 0.1 to 0.5 grs per sheet.

Anionic fluorescent brightening agents are well-known materials, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino) stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino) stilbene-2:2'-di-sulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino) stilbene-2,2'-di-sulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis(2'-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, sodium 2(stilbyl-4"-(naphtho-1',2':4,5)-1,2,3-triazole-2"-sulphonate and di-sodium 4,4'-bis(2-sulphonato styryl)biphenyl.

Other fluorescers to which the invention can be applied include the 1,3-diaryl pyrazolines and 7-alkylaminocoumarins.

A preferred fluroescer is the anionic material available from Ciba Geigy S.A. under the trade name Tinopal CBS and mixtures thereof with materials available under the trade names Tinopal EMS and Blankophor MBBN, the latter being sold by Farbenfabriken Bayer AG.

Other preferred optional ingredients include the multifunctional photoactivator/dyes belonging to the porphine class of general formula



- wherein each X is (=N-) or (=CY-), and the total number of (=N-) groups is 0, 1, 2, 3 or 4; wherein each Y, independently, is hydrogen or meso substituted alkyl, cycloalkyl, aralkyl, aryl, alkaryl or heteroaryl; wherein each R, independently, is hydrogen or pyrrole substituted alkyl, cycloalkyl, aralkyl, aryl, alkaryl or heteroraryl, or wherein adjacent pairs of R's are joined together with orthoarylene groups to form pyrrole substituted alicyclic or heterocyclic rings; wherein A is 2(H) atoms bonded to diagonally opposite nitrogen atoms, or Zn(II), Cd(II), Mg(II), Ca(II), Al(III), Sc(III), or Sn(IV); wherein B is an anionic, nonionic or cationic solubilizing group substituted into Y or R; wherein M is a counterion to the solubilizing groups; wherein, when B is cationic, M is an anion and s is from 1 to 8; when B is nonionic, B is polyethoxylate, M is zero, s is from 1 to 8, and the number of condensed ethylene oxide molecules per porphine molecule is from 8 to 50; when B is anionic and proximate, M is cationic and s is from 3 to 8; when B is anionic and remote, M is cationic and s is from 2 to 8; and when B is sulphonate the number of sulphonate groups is no greater than the number of aromatic and heterocyclic substituent groups.

As used herein, a solubilizing group attached to a carbon atom displaced more than 5 carbon atoms away from the porphine core is referred to as "remote"; otherwise it is "proximate".

Highly preferred materials of this general type are the zinc phthalocyanine tri- and tetrasulphonates and mixtures thereof. Materials of this general class were originally disclosed for use in detergent compositions in British
5 Patents 1,372,035 and 1,408,144 and are discussed in detail in European Patent Application 3861. The photo-activators can provide bleaching effects on fabrics washed with the detergent additive compositions and dried in the presence of visible light and atmospheric oxygen and can also
10 synergistically enhance the bleaching effect of conventional bleaching agents such as sodium perborate. The porphine bleach is preferably used in an amount such that the level of porphine in the composition is in the range from 0.004% to 0.5%, more preferably from 0.001% to 0.1%, especially from
15 0.002% to 0.05% by weight.

Preferred enzymatic materials include the commercially available amylases, and neutral and alkaline proteases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and
20 3,533,139. Examples of suitable enzymes include the materials sold under the Registered Trade Marks Maxatase, Rapidase and Alcalase.

As stated previously most of the above-mentioned functional ingredients, with the exception of the nonionic
25 surfactants, the organic suds modifiers and certain anti-redeposition agents, are solid materials which form the dispersed particulate phase of the detergent compositions. The particulates are insoluble, or only partly soluble, in the solidified liquid phase and ideally are finely divided.
30 Their particle size should be no more than $150\mu\text{m}$ and preferably should be less than $100\mu\text{m}$, ideally less than $50\mu\text{m}$.

Preferred detergent compositions useful in the present invention include one or more of a cationic surfactant as
35 hereinbefore defined, most preferably of the type where Y is $\begin{array}{c} | \\ -\text{N}^+ \\ | \end{array}$ and m is 1 or 2, a chelating agent of the amino polyphosphonate type particularly EDTMP or DETPMP and a

peroxyacid bleach precursor of the tetracetyl alkylene
diamine and/or $C_1 - C_9$ acyloxybenzene sulphonic or
carboxylic acid type, together with a $C_8 - C_{22}$ ethoxylated
primary alcohol and a polyethylene glycol of Mwt 4,000 -
5 10,000.

The types and levels of the ingredients of the detergent
composition is constrained by the requirements of mutual
unreactivity (if the materials are applied so as to be in
intimate contact), by the weight ratio of components forming
10 particulate solids to components forming the solidified
liquid phase and by the loading limitations of the
substrate. As mentioned above, materials that are capable of
mutual reaction can be incorporated in the additive products
of the invention, but must be spatially separated from each
15 other i.e. by application to a substrate location that is
free or substantially free of the other reactant
material(s). The detergent composition is preferably
applied, as described in more detail hereinafter, as a molten
dispersion to the substrate so that the maximum viscosity
20 that can be handled by the application system determines the
maximum level of dispersed particulate solids in the
composition. This level is generally approximately 50% by
weight. The minimum level of 5% by weight of the
composition is less critical. Preferably the level of
25 dispersed particulate solids is from 25% to 45% by weight of
the composition.

Within the limits imposed by the ratio of particulate
solid to solidified liquid components, individual components
can be incorporated in amounts up to those corresponding to
30 component:substrate weight ratios of 10:1. However, for
processing and product aesthetics reasons, the total weight
of particulate components per sheet is normally held to a
maximum of 4 times the sheet weight, and individual
components are ideally present at no more than 3 times the
35 sheet weight.

The detergent compositions useful in the invention also comprise a solidified liquid phase in which the solid particles are dispersed. As mentioned above certain functional components of the composition such as nonionic
5 surfactants can act as the, or part of the, solidified liquid phase but in general the majority of the solidified liquid phase is a water soluble or water dispersible processing aid having a melting point in the range from 30°C to 80°C. The most preferred processing aids are organic compounds having a
10 softening point greater than 40°C and a melting point less than 80°C to permit their easy processing.

These compounds serve as an aid in processing and/or in releasing the composition from the substrate when the latter is introduced into a wash liquor and, when melted, provide
15 mixtures having a viscosity of up to 5000 centipoises at 50°C.

Typical solids are C₁₄-C₁₈ primary and secondary alcohols and C₁₂-C₂₀ fatty acids and ethoxylates thereof containing from 15 to 80 ethylene oxide groups per mole of alcohol, sorbitan esters of C₁₂-C₂₀ fatty acids and
20 polyethylene glycols of Mwt 4000-10,000. Insoluble waxy materials such as paraffin waxes and alkyl fatty acid esters can also be used in minor amounts in admixture with one or more water soluble materials. Mixtures of the above water soluble materials are preferred.

As indicated above, the organic compounds forming the solidified liquid phase can serve as a release aid that assists in releasing the compositions from the substrate upon addition of the product to a wash liquor. In general, materials serving as processing aids are also suitable as
25 release aids but certain materials, notably C₁₆-C₁₈ fatty acids and polyethylene glycols of Mwt 4,000-10,000, are particularly effective when used in amounts such that the weight ratio of compositions:release aid lies in the range
30 9:1 to 1:1 particularly 3:1 to 1:1.

It will be apparent that the detergent compositions of the additive products in accordance with the invention will incorporate a high level of organic material having a Mpt > 30°C and this will include at least 50% by weight of the composition of carrier material having a melting point in the range 30°C-80°C either in the form of a processing aid or as one of the functional detergent components. Typically the composition will incorporate at least 55% of such carrier materials and, depending on the nature and physical characteristics of the "non-carrier" solid components, the level of carrier materials may be as high as 70% of the composition.

The substrate may itself be water soluble or water insoluble and in the latter case it should preferably possess sufficient structural integrity under the conditions of the wash to be recovered from the machine at the end of the laundry cycle. Water soluble materials include certain cellulose ethers, alginates, polyvinyl alcohol and water soluble polyvinyl pyrrolidone polymers, which can be formed into non-woven and woven fibrous structures. Suitable water insoluble materials include, but are not restricted to, natural and synthetic fibres, foams, sponges and films.

Preferably the sheet is water pervious i.e. water can pass from one surface of the sheet to the opposite surface and, for film type substrates, perforation of the sheet is desirable. The most preferred form of the substrate is a sheet of woven or non-woven fabric or a thin sheet of cellular plastics material. Woven fabric sheets can take the form of a plain weave natural or synthetic fibre of low fibre count/unit length, such as is used for surgical dressings, or of the type known as cheese cloth. Loading limitations on sheet type substrates limit the amount of detergent

composition that can be applied to the sheet namely to a maximum represented by a precursor:sheet weight ratio of about 10:1.

5 A very desirable attribute of the laundry additive products of the present invention is that they do not interfere with the mechanical operation of the washing machine into which they are put. A high proportion of domestic washing machines are of the rotating perforated drum type in which the perforations extend over the entire
10 peripheral surface. In this type of equipment the drum construction and mode of operation obviates any problem of obstruction to liquid flow in the machine. Certain older types of machine utilise an agitator in a stationary vessel provided with a recirculating liquid system. In order to
15 avoid liquid blockage in this machine type it may be necessary to provide slits or perforations in the substrate, particularly if it is in sheet form. Sheet structures of this type are disclosed in McQueary US Patents Nos. 3944694 and 3956556 issued March 16, 1976 and May 11, 1976
20 respectively.

As stated above, suitable materials which can be used as a substrate in the invention herein include, among others, sponges, paper, and woven and non-woven fabrics.

25 A suitable sponge like material that can be used in the present invention comprises an absorbent foam like material in the form of a sheet. The term 'absorbent foam-like material' is intended to encompass three dimensional absorptive materials such as 'gas blown foams', natural sponges and composite fibrous based structures such as are
30 disclosed in US Patent Nos. 3311115 and 3430630. A particularly suitable material of this type is a hydrophilic polyurethane foam in which the internal cellular walls of the foam have been broken by reticulation. Foams of this type are described in detail in Dulle US Patent No. 3794029. A
35 preferred example of this foam type comprises a hydrophilic polyurethane foam of density 0.596 grs per cubic inch with a

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cell count of between 8 and 40 cells per cm, preferably about 24 to 32 per cm available from the Scott Paper Company, Eddystone, Pennsylvania USA., under the Registered Trade Mark "Hydrofoam". Preferred sheets of this type of material have
5 thicknesses in the range from 3 to 5 mm.

A suitable paper-based absorbent structure containing 2 or 3 paper plies is disclosed in USP 3414459.

The preferred substrates of the laundry additive products of the invention are apertured and non apertured nonwoven
10 fabrics which can generally be defined as adhesively bonded fibrous or filamentous products, having a web or carded fibre structure (where the fibre strength is suitable to allow carding) or comprising fibrous mats, in which the fibres or filaments are distributed haphazardly or in random array
15 (i.e. an array of fibres in a carded web wherein partial orientation of the fibres is frequently present as well as a completely haphazard distributional orientation) or substantially aligned. The fibres or filaments can be natural (e.g. wool, silk, wood pulp, jute, hemp, cotton,
20 linen, sisal, or ramie), synthetic (e.g. rayon, cellulose, ester, polyvinyl derivatives, polyolefins, polyamides, or polyesters) or mixtures of any of the above.

Methods of making non-woven cloths are not a part of this invention and being well known in the art, are not described
25 in detail herein. Generally, such cloths are made by air or water laying processes in which the fibres or filaments are first cut to desired lengths from long strands, passed into a water or air stream, and then deposited onto a screen through which the fibre-laden air or water is passed. The deposited
30 fibres or filaments are then adhesively bonded together, dried, cured and otherwise treated as desired to form the non-woven cloth. Non-woven cloths made of polyesters, polyamides, vinyl resins, and other thermoplastic fibres can be bonded, i.e. the fibres are spun out onto a flat surface
35 and bonded (melted) together by heat or by chemical reactions.

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The absorbent properties desired herein are particularly easy to obtain with non-woven cloths and are provided merely by building up the thickness of the cloth, i.e. by super-imposing a plurality of carded webs or mats to a thickness adequate to obtain the necessary absorbent properties, or by allowing a sufficient thickness of the fibres to deposit on the screen. Any diameter or denier of the fibre (generally up to about 10 denier) can be used, inasmuch as it is the free space between each fibre that makes the thickness of the cloth directly related to the absorbent capacity of the cloth, and which further makes the non-woven cloth especially suitable for impregnation with a peroxy compound detergent composition by means of interstitial or capillary action. Thus, any thickness necessary to obtain the required absorbent capacity can be used.

The choice of binder-resins used in the manufacture of non-woven cloths can provide substrates possessing a variety of desirable traits. For example, the absorbent capacity of the cloth can be increased, decreased, or regulated by respectively using a hydrophilic binder-resin, a hydrophobic binder-resin or a mixture thereof in the fibre bonding step. Moreover, the hydrophobic binder-resin, when used singly or as the predominant compound of a hydrophobic-hydrophilic mixture, provides non-woven cloths which are especially useful as substrates when the detergent composition-substrate combinations disclosed herein are used in an automatic washer.

When the substrate herein is a bonded non-woven cloth made from fibres, deposited haphazardly or in random array on the screen, the compositions exhibit excellent strength in all directions and are not prone to tear or separate when used in the washer.

Preferably, the non-woven cloth is water-laid or air-laid and is made from cellulosic fibres, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant. Preferably the fibres are from 4 to 50 mm in length and are from 1.5 to 5 denier (Denier is an

internationally recognised unit in yarn measure,
corresponding to the weight in grams of a 9,000 meter length
of yarn). Preferably the fibres are at least partially
orientated haphazardly, particularly substantially
5 haphazardly, and are adhesively bonded together with
hydrophobic or substantially hydrophobic binder-resin,
particularly with a nonionic self-crosslinking acrylic
polymer or polymers. Conveniently, the cloth comprises 70%
fibre and 30% binder-resin polymer by weight and has a basis
10 weight of from 10 to 100, preferably from 24 to 72 g/m².

A suitable example is an air-laid, non-woven cloth
comprising 70% regenerated cellulose (American Viscose
Corporation) and 30% hydrophobic binder-resins (Rhoplex HA-8
on one side of the cloth, Rhoplex HA-16 on the other; Rohm &
15 Haas, Inc). The cloth has a thickness of 4 to 5 mils., a
basis weight of 29 g/m². A 30 cm length of the cloth 21 cm
wide weighs 1.78 grams. The fibres are 10 mm in length, 1.5
denier, and are orientated substantially haphazardly. The
fibres are lubricated with sodium oleate.

A further exemplary substrate is a water-laid, non-woven cloth commercially available from C H Dexter Co., Inc. The fibres are regenerated cellulose, 15 mm in length, 1.5 denier, and are lubricated with a similar standard textile lubricant. The fibres comprise 70% of the non-woven cloth by weight and are orientated substantially haphazardly; the binder-resin (HA-8) comprises 30% by weight of the cloth. The substrate is 4 mils thick, and it has a basis weight of 29 g/m^2 . A 30 cm length of the cloth 21 cm wide, weighs 1.66 grams.

Apertured non-woven substrates are also useful for the purposes of the present invention. The apertures, which extend between opposite surfaces of the substrate are normally in a pattern and are formed during lay-down of the fibres to produce the substrate. Exemplary apertured non-woven substrates are disclosed in US Patent Nos. 3,741,724, 3,930,086 and 3,750,237.

A suitable diamond patterned apertured substrate is obtainable from Chicopee Manufacturing Co., Milltown, New Jersey, USA under the Code No. SK 650 WFX 577 and comprising a polyester-wood pulp mixture having a basis weight of 50 g/m^2 and approximately 13 apertures per square cm.

Another preferred example of an apertured non-woven substrate, also available from Chicopee Manufacturing Co., under the Code No. AK 30 ML 1379 comprises a regenerated cellulose sheet of 3.0 denier fibres bonded with Rhoplex RA 8 binder (fibre:binder ratio 70:30) having a basis weight of 40 g/m^2 and 17 apertures/ cm^2 . A highly preferred square patterned apertured substrate of similar composition but fibre:binder ratio of 80:20 and basis weight 35 g/m^2 is also available from Chicopee BV Holland.

In general, apertured fabrics for the purposes of the invention have from 10-20 apertures/ cm^2 , preferably 12-18 apertures/ cm^2 .

The size and shape of the substrate sheet is a matter of choice and is determined principally by factors associated with the convenience of its use. Thus the sheet should not

be so small as to become trapped in the crevices of the machine or the clothes being washed or so large as to be awkward to package and dispense from the container in which it is sold. For the purposes of the present invention sheets
5 ranging in plan area from 130 cm^2 to 1300 cm^2 are acceptable, the preferred area lying in the range of from 650 cm^2 to 900 cm^2 .

The invention is illustrated in the following examples in which all parts and percentages are by weight of the
10 composition unless otherwise specified.

In the Examples, the abbreviations used have the following designation:

	$\text{C}_{14/15} \text{ AS}$: Sodium $\text{C}_{14}\text{-C}_{15}$ alkyl sulphate
	$\text{C}_{12/14} \text{ AS}$: Sodium $\text{C}_{12}\text{-C}_{14}$ alkyl sulphate
15	TAE_n	: Tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol
	$\text{C}_{14} \text{ TMAB}$: C_{14} alkyl trimethyl ammonium bromide
20	$\text{C}_{10} \text{ TMAMS}$: C_{10} alkyl trimethyl ammonium methyl sulphate
	$\text{C}_{12} \text{ TMAB}$: C_{12} alkyl trimethyl ammonium bromide
	A 45-E-7	: A $\text{C}_{14}\text{-15}$ primary alcohol condensed with 7 moles of ethylene oxide.
25	PEG	: Polyethylene glycol (Mwt normally follows)
	TAED	: Tetraacetyl ethylene diamine
	PAG	: Penta acetyl glucose
	DIGOL	: Diethylene glycol
	PRODIOL	: 1,2-propane diol

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	Silicone Compound:	85% polydimethyl siloxane 15% silica
5	MVEMA	Maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of 240,000. This material was prehydrolysed with NaOH before addition.
	Perborate monohydrate	: Anhydrous sodium perborate bleach of empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
10	Enzyme	: Mixed proteolytic and amylolytic enzyme sold by Novo Industrie AS.
	EDTA	: Sodium ethylene diamine tetra acetate
	Brightener 1	: Disodium 4,4'-bis(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2:2'-disulphonate.
15	Brightener 2	: Disodium 4,4'-bis(2-sulphonato styryl)biphenyl
	DETPMP	: Diethylene triamine penta(methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
20	EDTMP	: Ethylenediamine tetra (methylene phosphonic acid), marketed by Monsanto, under the Trade name Dequest 2041
25	H ₂ O ₂ Clathrate	: A clathrate of $4\text{Na}_2\text{SO}_4$: $2\text{H}_2\text{O}_2$: 1NaCl

EXAMPLE 1

The following product was prepared:

C

	TAED	5.0g
30	A 45E7	5.0g
	PEG 8000	5.0g
	C ₁₄ TMAB	2.0g
	EDTMP	0.5g
	MVEMA	0.3g
35	Glycerol	0.3g
	Silicone Compound	0.25g
	Brightener 2	0.1g
	Perfume	0.08g
	Substrate	2.8g

The substrate was a square patterned apertured non-woven sheet, of size 23 x 35 cm and basis weight 2.8 g, formed of 100% unbleached crimped rayon fibres (80% fibre, 20% polyacrylate binder). The product was made by forming a melt
5 of the PEG and A 45E7 at approximately 80°C, dispersing the other components (except the perfume) therein and applying the resultant slurry to the substrate from an applicator roll with which the substrate was brought into contact. Additional rolls were used to spread the slurry before it was
10 cooled to ambient temperature to solidify the composition. Perfume was then sprayed on to the impregnated substrate to produce the final product.

No appreciable build up of product was noted on the processing equipment and the product demonstrated virtual
15 freedom from flaking (i.e. a flaking grade of 9+) when it was folded. Similar results are obtained if the glycerol is replaced by 0.3g diethylene glycol or by 0.3g 1-2 propane diol.

EXAMPLES 2-10

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The following products, in accordance with the invention,
are prepared (in parts by weight):

	2	3	4	5	6	7	8	9	10
TAED			5.0					3.5	3.5
5 PAG		4.2				3.9		4.2	4.2
Glycerol	0.3		0.3	0.3		0.3			0.3
1-2 PRODIOL		0.3					0.3		
DIGOL					0.3			0.3	
Perborate Monohydrate	2.0			3.9	3.6		4.0		
10 H ₂ O ₂ Clathrate						4.5			
EDTA				1.0	1.0				
EDIMP	0.5	0.5				0.5	0.5		0.5
DEDIMP			0.5					0.5	
15 A 45E7	5.0	5.0	5.0		2.0	5.0			5.0
C ₁₂ -C ₁₄ AS	3.0			3.0					
C ₁₄ -C ₁₅ AS					4.0				
TAE ₂₅			2.0	2.5				3.0	
C ₁₀ TMAMS				3.0					
20 C ₁₂ TMAB			2.0		2.0				
C ₁₄ TMAB	2.0	2.0				2.0		2.0	2.0
PEG 8000	5.0	5.0	3.0	6.0	7.0	6.0	5.0	5.0	5.0
Silicone Compound	0.25	0.25	0.2	0.1		0.1			0.25
25 MVEMA	0.35	0.35	0.3					0.3	0.35
Enzyme	0.8		0.8	0.9	0.9	0.9		0.6	0.6
Brightener 1				0.1	0.1				
Brightener 2	0.1	0.1	0.1			0.1		0.1	0.1
Perfume	0.1	0.1	0.1	0.1		0.1		0.1	0.1
30 Substrate	2.8	2.8	2.8	2.8	2.8	2.8	0.9	2.8	2.8

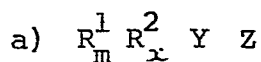
CLAIMS

1. A laundry additive product comprising a normally solid detergent composition comprising a solidified liquid matrix having a melting point greater than 30°C and less than 80°C,
 5 in which matrix is dispersed solid particles of size 150 μ m, said solid particles comprising from 5% to 50% by weight of the composition, said composition being in water releasable combination with a flexible sheet substrate, the weight ratio of said composition to said substrate lying in the range from
 10 1:2 to 12:1 characterised in that said composition includes a liquid processing aid selected from polyols of MWt \leq 180 and boiling point (at a pressure of 760 mm Hg) of at least 100°C in an amount of from 0.5% to 5.0% by weight of the composition.

15 2. A laundry additive product according to Claim 1 wherein the polyol is selected from glycerol, diethylene glycol, 1,2-propane diol and 2-methyl propane 1-2 ol.

3. A laundry additive product according to either one of Claims 1 and 2 wherein the polyol is present in an amount of
 20 from 0.5% to 3.0% by weight of the composition.

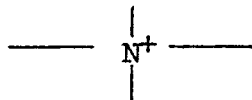
4. A laundry additive product comprising a detergent composition composed of an organic matrix having a melting point greater than 30°C and less than 80°C, said matrix comprising a mixture of a polyethylene glycol of MWt 4,000 -
 25 10,000 and a primary C₈ - C₂₂ aliphatic alcohol condensed with an average of from 4 to 30 moles of ethylene oxide, said matrix forming a solidified liquid phase in which are dispersed solid particles of a compound selected from:



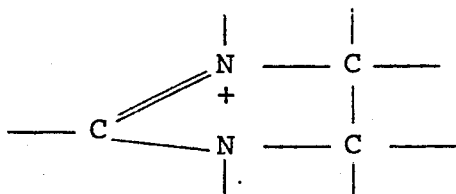
wherein each R¹ is a hydrophobic organic group containing
 30 alkyl chains, alkenyl chains, alkyl benzyl chains, alkyl phenyl chains, ether linkages, alkylene groups, alkenylene groups, ester linkages, and amide linkages totalling from 8

to 22 carbon atoms and which may additionally contain or be attached to a polyethylene oxide chain containing up to 20 ethoxy groups, m is a number from one to three provided that no more than one R^1 in a molecule can have more than 16 carbon atoms when m is 2 and no more than 12 carbon atoms when m is 3, R^2 is an alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms or a benzyl group, with no more than one R^2 in a molecule being benzyl, and x is a number from 1 to 3, Y is selected from

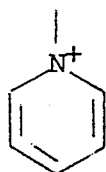
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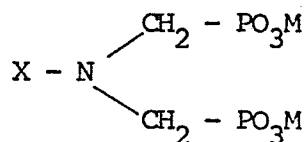


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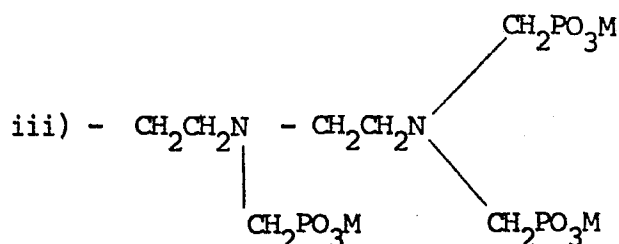
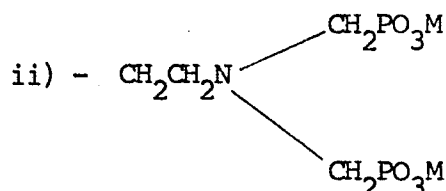


10 and Z is a water-soluble anion selected from halide, methosulphate, carboxylate, hydroxide, or nitrate

b)

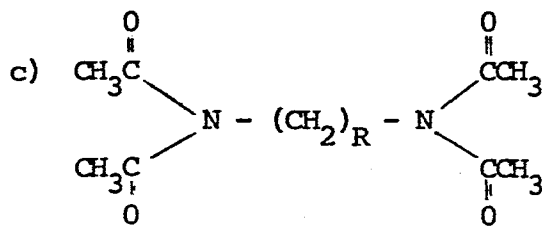


wherein X is i) - $\text{CH}_2\text{PO}_3\text{M}$

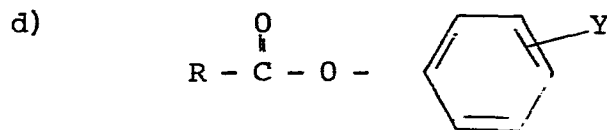


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wherein M is hydrogen or an alkali metal ion



where n is from 1 to 6



wherein R is C₁ - C₉ linear or branched alkyl

Y is SO₃M, COOH or COOM where

M is an alkali metal ion;

5

said solid particles comprising from 5% to 50% by weight of the composition, said composition being in water releasable combination with a flexible sheet substrate, the weight ratio of said composition to said substrate lying in the range from 1:2 to 12:1

10

characterised in that said composition includes a liquid processing aid selected from polyols of MWt ≤ 180 and boiling point (at a pressure of 760 mm Hg) of at least 100°C in an amount of from 0.5% to 5.0% by weight of the composition.



European Patent
Office

EUROPEAN SEARCH REPORT

0118191

Application number

EP 84 30 0542

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,A	GB-A-1 586 769 (PROCTER & GAMBLE LTD.) * Claims 1, 5 *		C 11 D 17/04
D,A	EP-A-0 013 450 (PROCTER & GAMBLE LTD.) * Claims 1, 6 *		
A	AU-B- 493 972 (CHURCH & DWIGHT CO.) * Claim 2 *		
A	EP-A-0 000 234 (PROCTER & GAMBLE CO.) * Claim 1 *		
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			C 11 D 1/00 C 11 D 3/00 C 11 D 17/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 30-04-1984	Examiner SCHULTZE D
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			