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(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
301 East Sixth Street
Cincinnati Ohio 45201(US)

(72) Inventor: **Talkes, Brian Edward**
Greystoke Howard Road
Morpeth Northumberland(GB)

(72) Inventor: **Cassidy, Stephen Paul**
6 Rosedale Cheviot Court Hadrian Lodge West
Wallsend Newcastle upon Tyne(GB)

(74) Representative: **Brooks, Maxim Courtney et al,**
Procter & Gamble (NTC) Limited Whitley Road
Longbenton
Newcastle-upon-Tyne NE12 9TS(GB)

(54) Laundry additive products.

(57) Laundry additive products comprising a solid laundry additive composition and a flexible, sheet-like apertured substrate carrying a water-releasable coating of the laundry additive composition. The substrate has an aperture density of from about 10 to 30 apertures per sq cm and the apertures have a width of from about 0.5 to 5mm and a length of from about 0.8 to 5mm. The product comprises areas of uncoated aperture and areas within the coating covers the apertures and extends between opposing surfaces of the substrate. The ratio of areas of uncoated to coated apertures is from about 15:1 to 1:3. The weight ratio of composition:substrate is at least 5:1. The additive products combine a high loading of composition together with excellent flexibility, product release, feel and storage characteristics.

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LAUNDRY ADDITIVE PRODUCTS

0096566

Brian Edward Talkes
Stephen Paul Cassidy

Technical Field

This invention relates to laundry additive products. In particular, it relates to laundry additive products for cleaning clothes or other fabrics or for providing an adjunct laundering benefit, the additive product comprising a water-insoluble substrate and a laundry-additive composition coated on or impregnated into the substrate.

Background

Laundry additive products based on water-insoluble substrates are now well known in the art. For example, US-A-3,422,692, Gaiser, issued May 6 1969 discloses a method for softening and controlling static on fabrics in a laundry washing machine or dryer using a fabric conditioning composition coated on a substrate. UK-A-1,586,769 teaches a laundry additive product containing an organic peroxy compound precursor combined with a solid article, particularly a sheet-like, water-insoluble substrate. US-A-4,170,565, Flesher et al, relates to an article for cleaning fabrics yielding sequential release of surface-active components, consisting of a surface-active composition contained between two layers of water-insoluble substrate of defined air permeability.

A key constraint of a substrate-based laundry-additive product, particularly for use as a detergent or detergent additive for washing clothes and the like, is the ability to load a relatively large amount of the laundry additive composition onto the substrate and simultaneously to achieve rapid and complete release of the additive composition during the course of the laundering operation. This is to be contrasted with articles of the cleaning cloth variety used in the washing and scrubbing of hard surfaces such as dishes and counter tops and which rely on physical rubbing and scrubbing during use to assure the release of the proper amount of cleansing composition for the cleaning operation. Such articles are generally designed for multiple repeated use and are formulated, therefore, to release only a small proportion of the total cleaning composition during any single use of the article.

To achieve rapid release of laundry additive composition, it is generally found desirable to utilize a substrate of low basis weight. Particularly acceptable from this viewpoint are single layer substrates impregnated with or carrying a coating of the laundry additive composition. As a result of high loading and low substrate basis weight, therefore, laundry additive products having optimum performance for general detergency use inevitably have a high composition:substrate weight ratio (referred to herein as loading ratio).

From the viewpoint of processing, product aesthetics, and storage characteristics, however, designing a laundry additive product having a high loading ratio raises a number of intractible problems. First and foremost, the flexibility of the substrate rapidly diminishes at high loading ratio and the product becomes increasingly rigid and board-like. Not only is this disliked by consumers but it also raises processing problems associated with composition flaking from the sheet, and manufacturing and packaging problems associated with folding the article into a form which is compact and convenient for use. Where, on the other hand, the additive composition is made sufficiently soft and plastic to mitigate flexbility problems, the articles become quite sticky and uncomfortable to touch and associated problems of handling and storage (blocking phenomena etc) become increasingly important.

It has now been found that by selecting certain laundry additive compositions of defined melting characterstics and certain sheet-like apertured substrates of defined aperture size and density and by coating the substrate so as to cover and fill only a defined proportion of the substrate apertures, laundry additive products can be provided which simultaneously meet the mutual constraints of high loading, good release characteristics, and excellent flexiblity and product feel characteristics.

The present invention thus provides a laundry additive product having a high composition:substrate ratio together with excellent product flexibility characteristics, which is not sticky to handle and which is easy to manufacture, use and store, and which can be used in a laundering operation to clean clothes and other fabrics effectively and conveniently or to provide additional laundering benefits.

Summary of the Invention

According to the present invention, there is provided a laundry additive product comprising:

(a) a solid laundry additive composition having a softening temperature of at least about 35°C and comprising at least about 40% of a water-soluble or water-dispersible matrix of organic materials having a melting completion temperature of less than about 85°C, and

(b) a flexible, sheet-like apertured substrate having an aperture density of from about 10 to about 30 apertures per sq cm of sheet and wherein the apertures, on average, have a width of from about 0.5mm to about 5mm and a length of from about 0.8mm to about 5mm, the substrate carrying a water releasable coating of the laundry additive composition and having areas of uncoated apertures and areas wherein the coating covers the apertures and extends between opposing surfaces of the substrate, the ratio of areas of uncoated to coated apertures being in the range from about 15:1 to about 1:3 and wherein the weight ratio of composition:substrate is at least about 5:1.

With regard to the substrate, this preferably has an aperture density of from about 13 to about 26, more preferably from about 16 to about 23 apertures per sq cm of sheet, a basis weight of from about 10 to about 70 grams/sq metre, more preferably from about 20 to about 50 grams/sq metre and a hydrophobic binder resins content of from about

12% to about 25%, more preferably from about 16% to about 22% by weight of total substrate. The apertures themselves are generally symmetrical about a longitudinal axis (ie they have mirror symmetry) and preferably have, on average, a width of from about 0.7 to about 2.5mm and a length of from about 1.7mm to about 4mm. The area of the apertures, on the other hand, is preferably from about 0.7mm^2 to about 7mm^2, more preferably from about 0.8mm^2 to about 3.5mm^2, and the ratio of length:width is from 1:1 up to preferably about 6:1, more preferably about 4:1. These parameters are highly preferred from the viewpoint of achieving the optimum ratio of areas of uncoated to coated apertures and the complete filling of coated apertures from one surface of the substrate to the other.

The substrate apertures herein can be elongate in shape (for example, generally elliptical or diamond-shaped) in which case the apertures preferably have a width of from about 0.8mm to about 1.5mm and a length of from about 2mm to about 3.5mm.In preferred embodiments, however, the apertures are generally square-shaped with a side dimension of from about 1 to 2.5mm. As used herein, "length" refers to the dimension of the principal (ie longest) longitudinal axis, and "width" is the maximum dimension perpendicular to this axis.

As far as loading ratio is concerned (ie the weight ratio of composition:substrate) this preferably is at least about 6:1 and more preferably at least 7:1. Moreover the ratio of the areas of uncoated to coated apertures in the final product is preferably from about 6:1 to about 1:2, more preferably from about 4:1 to about 1:1.

Turning to the laundry additive composition, this preferably comprises at least about 50%, more preferably at least about 60% of organic matrix materials; these in turn each preferably have a melting completion temperature of less than about 75°C, more preferably less than about 70°C. The laundry additive composition itself desirably has a

softening temperature of at least about 40°C, especially at least about 50°C.

In preferred embodiments, the laundry additive product contains at least about 5%, preferably at least about 15% by weight of composition of water-soluble or water-dispersible organic binding agent having a melting-onset temperature of at least 35°C and a melting completion temperature of less than about 85°C. Preferably, the binding agent is selected from polyethylene glycols of molecular weight greater than about 1000, C_{12}-C_{18} fatty acids and esters and amides thereof, polyvinyl pyrrolidone of molecular weight in the range from about 40,000 to about 700,000, and C_{14}-C_{24} fatty alcohols ethoxylated with from about 14 to about 100 moles of ethylene oxide.

Highly preferred from the viewpoint of optimum flexibility and feel characteristics combined with excellent water-dispersibility at high loading ratios are polyethyleneglycols having a molecular weight greater than about 4,000, preferably greater than about 7,000, these materials preferably comprising at least about 40%, more preferably at least about 50% of the organic binding agent.

The laundry additive products of the invention suitably contain at least about 5%, preferably at least about 20% of additive composition of organic detergent selected from anionic, nonionic and cationic surfactants and mixtures thereof. Preferred nonionic surfactants have melting completion temperatures of less than about 85°C and form part of the matrix of organic materials. Preferred cationic surfactants have melting onset temperatures of at least about 35°C and can form either part of the organic binding agent or can be dispersed in the organic matrix. Preferred anionic surfactants have melting completion temperatures in excess of about 100°C and are dispersed in the organic matrix.

Other functional solid imgredients can also be present as a dispersion in the organic matrix, especially inorganic or organic peroxy bleaches which preferably comprise at

least about 5% by weight of additive composition, and/or organic peroxy acid bleach precursors which preferably comprise at least about 2% by weight of additive composition. Other suitable functional ingredients include detergency enzymes, fluorescers, photoactivators, sequestrants, bleaching catalysts, and suds-controlling agents.

The laundry additive products of the invention will now be discussed in detail.

Preferred substrates for use herein are apertured nonwoven 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 (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, linen, sisal, or ramie), synthetic (e.g. rayon, cellulose, ester, polyvinyl derivatives, polyolefins, polyamides, or polyesters) or mixtures of any of the above.

Generally, non-woven 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 fibres or filaments are then adhesively bonded together, dried, cured and otherwise treated as desired to form the non-woven cloth.

Preferably, the non-woven cloth is made from cellulosic fibres, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant such as sodium oleate. Preferably the fibres are from about 4 to about 50 mm, especially from about 8mm to

about 20mm, in length and are from about 1 to about 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 haphazardly, and are adhesively bonded together with hydrophobic or substantially hydrophobic binder-resin, particularly with a nonionic self-crosslinking acrylic polymer or polymers. In highly preferred embodiments, the cloth comprises from about 75% to about 88%, especially from about 78% to about 84% fibre and from about 12% to about 25%, especially from about 16% to about 22% hydrophobic binder-resin polymer by weight and has a basis weight of from about 10 to about 70, preferably from 20 to 50 g/m^2. Suitable hydrophobic binder-resins are ethylacrylate resins such as Primal HA24 Rhoplex HA8 and HA16 (Rohm and Haas, Inc) and mixtures thereof.

The substrate 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.

An example of an apertured non-woven substrate suitable herein is a regenerated cellulose sheet of 1.5 denier fibres bonded with Rhoplex HA 8 binder (fibre:binder ratio of about 77:23) having a basis weight of about 35 g/m^2 and about 17 apertures/cm^2. The apertures are generally ellipitical in shape and are in side-by-side arrangement. The apertures have a width of about 0.9mm and a length of about 2.5mm measured in a relaxed condition. Another highly preferred substrate based on 1.5 denier regenerated cellulose fibres with Rhoplex HA8 binder has a fibre:binder ration of about 82:18, a basis weight of about 35g/m^2, and about 22 apertures/cm^2. In this example, the apertures are generally square-shaped with a width

(relaxed) of about 1.1mm. The apertures are again disposed in side-by-side arrangement.

The size and shape of the substrate sheet for each unit of product 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 ranging in plan area from about 130 cm^2 to about 1300 cm^2 are acceptable, the preferred area lying in the range of from about 520 cm^2 to about 780 cm^2.

Turning to the laundry additive composition, this is in solid form at ambient temperatures (25°C and below) and preferably has a softening temperature of at least about 35°C, more preferably at least about 40°C, especially at least about 50°C. By softening temperature is meant the temperature at which there is transition from plastic-flow to viscous-flow properties; at ambient temperatures, therefore, the composition takes the form of a plastic solid having a non-zero yield stress. The hardness of the compositions at ambient temperatures can be determined by standard methods, for example, by the penetrometer-based technique of IP49 (or the technically equivalent ASTM-D5 or BS4691). Thus, laundry additive compositions preferred for use herein have a penetration under a 100g load at 25°C after 15 seconds under IP49 of less than about 10 (measured in tenths of a millimetre), more preferably less than about 7. The softening temperature of the composition, on the other hand, is taken herein to be the temperature at which the IP49 15 second penetration exceeds about 30.

The laundry additive composition herein comprises a matrix of organic materials having defined melting characteristics. Melting completion temperatures are determined using a Dupont 910 Differential Scanning Calorimeter with Mechanical Cooling Accessory and R90 Thermal Analyser as follows. A 5-10 mg sample of the organic material containing no free water or solvent is encapsulated in a hermetically sealed pan with an empty pan as reference. The sample is initially heated until molten and then rapidly cooled (at about 20-30°C/min) to -70°C. Thermal analysis is then carried out a a heating rate of 10°C/min using sufficient amplification of ΔT signal (ie temperature difference between sample and reference - vertical axis) to obtain an endotherm-peak signal:baseline noise ratio of better than 10:1. The melting completion temperature is then the temperature corresponding to the intersection of the tangential line at the steepest part of the endotherm curve at the high temperature end of the endotherm, with the horizontal line, parallel to the sample temperature axis, through the highest temperature endotherm peak.

The organic materials constituting the matrix have a melting completion temperature of less than about 85°C. In addition, the laundry additive products of the invention preferably contain at least about 5% by weight of composition of binding agent defined as organic material having a melting completion temperature of less than 85°C, preferably less than about 80°C, especially less than about 70°C, and a melting onset temperature of at least 35°C, preferably at least 40°C, especially at least 50°C. The melting onset temperature can once again be determined by thermal analysis as described above and is taken to be the sample temperature at the point of intersection of the base line with a tangent to the steepest part of the endotherm nearest the low temperature end of the endotherm.

The laundry additive products of the invention can be supplemented by all manner of laundering and detergency components. Suitably, the additive products can contain

from about 5% to about 100%, preferably from about 20% to about 100%, more preferably from about 35% to about 75% of organic detergent selected from anionic, nonionic and cationic surfactants and mixtures thereof. Anionic surfactants preferably comprise from about 7% to about 38%, more preferably from about 15% to about 30% by weight of composition; nonionic surfactants from about 8% to about 32%, more preferably from about 12% to about 25% by weight of composition; and cationic surfactants from about 5% to about 30%, more preferably from about 8% to about 20% by weight of composition.

The anionic surfactant can be any one or more of the materials used conventionally in laundry detergents. Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulphonates, alkyl sulphates, alkyl polyethoxy ether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulpho-carboxylates and their esters, alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, alkyl phenol polyethoxy ether sulphates, 2-acyloxy alkane-1-sulphonate, and beta-alkyloxy alkane sulphonate.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents which form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C_{8-18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from about 9 to about 15, especially about 11 to about 13, carbon atoms, in straight chain or branched chain configuration,

e.g. those of the type described in U.S.P. 2,220,099 and 2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS, and C_{12}-C_{15} methyl branched alkyl sulphates.

Other anionic detergent compounds herein include the sodium C_{10-18} alkyl glyceryl ether sulphonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulphonates and sulphates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulphate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts or esters of α-sulphonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulphonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulphates containing from about 10 to 18, especially about 12 to 16, carbon atoms in the alkyl group and from about 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulphonates containing from about 12 to 24, preferably aout 14 to 16, carbon atoms, especially those made by reaction with sulphur trioxide followed by neutralization under conditions such that any sultones present are hydrolysed to the corresponding hydroxy alkane sulphonates; water-soluble salts of paraffin sulphonates containing from about 8 to 24, especially 14 to 18 carbon atoms, and β-alkyloxy alkane

sulphonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred. Suitable fatty acid soaps can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24, preferably from about 10 to about 22 and especially from about 16 to about 22 carbon atoms in the alkyl chain. Suitable fatty acids can be obtained from natural sources such as, for instance, from soybean oil, castor oil, tallow, whale and fish oils, grease, lard and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Napthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulfonate and sulfate surfactants in a weight ratio of from about 5:1 to about 1:5, preferably from about 5:1 to about 1:1, more preferably from about 5:1 to about 1.5:1. Especially preferred is a mixture of an alkyl benzene sulfonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal, preferably sodium; and either an alkyl sulfate having from 10 to 20,

preferably 12 to 18 carbon atoms in the alkyl radical or an ethoxy sulfate having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6, having an alkali metal cation, preferably sodium.

The nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from about 8 to 17, preferably from about 9.5 to 13.5, more preferably from about 10 to about 12.5. The hydrophobic moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. 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, the said ethylene oxide being present in amounts equal to 3 to 30, preferably 5 to 14 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 9 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and di-isooctylphenol condensed with 13 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 2 to about 40 moles, preferably 2 to about 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3

and 8 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Lutensols, Dobanols and Neodols which have about 25% 2-methyl branching (Lutensol being a Trade Name of BASF, Dobanol and Neodol being Trade Names of Shell), or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-9, Dobanol 91-2.5, Dobanol 91-3, Dobanol 91-4, Dobanol 91-6, Dobanol 91-8, Dobanol 23-6.5, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 15 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.3.

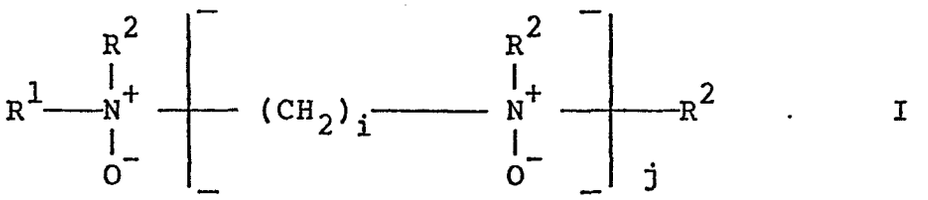
The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the Trade Name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

Especially preferred nonionic surfactants for use herein are the C_9-C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol,

particularly the C_{12}-C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants and surfactants of a semi-polar nature, for example amine oxides.

Suitable surfactants of the amine oxide class have the general formula I



I

wherein R^1 is a linear or branched alkyl or alkenyl group having 8 to 20 carbon atoms, each R^2 is independently selected from C_{1-4} alkyl and $-(C_nH_{2n}O)_mH$ where i is an integer from 1 to 6, j is 0 or 1, n is 2 or 3 and m is from 1 to 7, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 7.

In a preferred embodiment R^1 has from 10 to 14 carbon atoms and each R^2 is independently selected from methyl and $-(C_nH_{2n}O)_mH$ wherein m is from 1 to 3 and the sum total of $C_nH_{2n}O$ groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment, j is O and each R^2 is methyl, and R^1 is C_{12}-C_{14} alkyl.

Another suitable class of amine oxide species is represented by bis-amine oxides having the following substituents.

j : 1

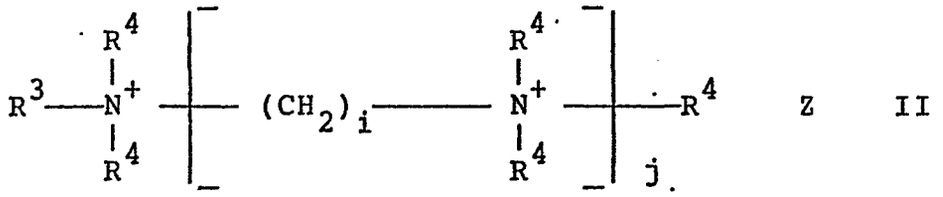
R^1: tallow C_{16}-C_{18} alkyl; palmityl; oleyl; stearyl

R_2: hydroxyethyl

i : 2 or 3

A specific example of this preferred class of bis-amine oxides is: N-hydrogenated C_{16}-C_{18} tallow alkyl-N,N',N'tri-(2-hydroxyethyl) -propylene-1,3-diamine oxide.

Suitable quaternary ammonium surfactants for use in the present composition can be defined by the general formula II:



Z II

wherein R^3 is a linear or branched alkyl, alkenyl or alkaryl group having 8 to 16 carbon atoms and each R^4 is independently selected from C_{1-4} alkyl, C_{1-4} alkaryl and $-(C_nH_{2n}O)_m$ wherein i is an integer from 1 to 6, j is 0 or 1, n is 2 or 3 and m is from 1 to 7, the sum total of $C_nH_{2n}O$ groups in a molecule being no more than 7, and wherein Z represents counteranion in number to give electrical neutrality.

In a preferred embodiment, R^3 has from 10 to 14 carbon atoms and each R^4 is independently selected from methyl and $(C_nH_{2n}O)_mH$ wherein m is from 1 to 3 and the sum total of $C_nH_{2n}O$ groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment j is 0, R^4 is selected from methyl, hydroxyethyl and hydroxypropyl and R^3 is C_{12}-C_{14} alkyl. Particularly preferred surfactants of this class include C_{12} alkyl trimethylammonium salts, C_{14} alkyltrimethylammonium salts, coconutalkyltrimethylammonium salts, coconutalkyldimethyl-hydroxyethylammonium salts, coconutalkyldimethylhydroxy-propylammonium salts, and C_{12} alkyldihydroxyethylmethyl ammonium salts.

Another group of useful cationic compounds are the diammonium salts of formula II in which j is 1, R^3 is C_{12}-C_{14} alkyl, each R^4 is methyl, hydroxyethyl or hydroxypropyl and i is 2 or 3. In a particularly preferred surfactant of this type, R^3 is coconut alkyl, R^4 is methyl and i is 3.

The laundry additive products of the invention can also include various functional solid ingredients dispersed

in the organic matrix, especially peroxy bleaches and organic peroxy acid bleach precursors. Suitable inorganic peroxygen bleaches include sodium perborate mono- and tetrahydrate, sodium percarbonate, sodium persilicate and urea-hydrogen peroxide addition products and the clathrate $4Na_2SO_4$: $2H_2O_2$:1NaCl. Suitable organic bleaches include peroxylauric acid, peroxyoctanoic acid, peroxynonanoic acid, peroxydecanoic acid, diperoxydodecanedioic acid, diperoxyazelaic acid, mono- and diperoxyphthalic acid and mono- and diperoxyisopthalic acid. Peroxyacid bleach precursors suitable herein are disclosed in UK-A-2040983, highly preferred being peracetic acid bleach precursors such as tetraacetylethylenediamine, tetraacetylmethylenediamine, tetraacetylhexylenediamine, sodium p-acetoxybenzene sulphonate, tetraacetylglycouril, pentaacetylglucose, octaacetyllactose, and methyl O-acetoxy benzoate. Bleach precursors can be applied to substrate at a precursor: substrate ratio within the range from about 30:1 to about 1:10, preferably from about 8:1 to about 1:2, while bleaches can be applied to substrate at a bleach:substrate ratio from about 30:1 to about 1:4, preferably from about 10:1 to about 1:1. For improved stability, the bleach precursor and bleach can be incorporated in physically separate locations of the substrate.

The compositions of the invention can be supplemented by all manner of other laundering ingredients, including suds controlling agents, fluorescers, photoactivators, enzymes, sequestrants, fabric softeners and antistatic agents, soil suspending agents etc, either as part of the matrix of organic materials or as a dispersion therein.

Suitable suds controlling agents include microcrystalline waxes having a melting point in the range from about 65°C to about 100°C, a molecular weight in the range from about 400-1000, and a penetration value of at least 6, measured at 77°C by ASTM-D1321; silicone suds controlling agent as disclosed in US 3,933,672, particularly polydimethylsiloxanes having a molecular weight in the range from about 200 to about 200,000 and a kinematic viscosity in the range from

about 20 to about 2,000,000 mm^2/s preferably from about 3000 to about 30,000 mm^2/s and mixtures of siloxanes and hydrophobic silanated (preferably trimethylsilanated) silica having a particle size in the range from about 10 millimicrons to about 20 millimicrons and a specific surface area above about 50 m^2/g; and the self emulsifying suds suppressors described in DE-A-2,646,126.

Suitable fluorescers herein include Blackophor MBBH (Bayer AG) and Tinopal CBS and EMS (Ciba Geigy). Suitable photoactivators are disclosed in European Application No 82300309, highly preferred materials being zinc phthalocyanine tri- and tetrasulphonates.

Chelating agents that can be incorporated include citric 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; 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 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 from about 20:1 to about 1:5, preferably from about 5:1 to about 1:5 and most preferably 3:1 to 1:1.

Antiredeposition and soil suspension agents also constitute preferred components of the additive product of

the invention. Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose are examples of soil suspension agents and suitable antiredeposition agents are provided by homo- or co-polymeric polycarboxylic acids or their salts in which at least two carboxyl radicals are present separated by not more than two carbon atoms.

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

A further description of suitable polymeric polycarboxylic acids is provided in the Applicants' European Patent Application No. 82301776.9.

In a method of making the laundry-additive products of the invention, a current of molten laundry-additive composition is dispensed onto moving substrate at an application rate of from about 100 to about 400 g/m^2, preferably from about 120 to about 320 g/m^2 of substrate, so as to coat no more than about 70%, preferably no more than about 45% of the apertures of the substrate. Thereafter, the coated substrate is passed through smoothing and distributing means arranged to smooth and distribute the coating on the substrate with substantially no removal of coating material from off the substrate.

The temperature of the melt generally lies in the range from about 35°C to about 85°C, preferably from about 40°C to abut 75°C, more preferably from about 50°C to about 70°C and the average particle size of solids dispersed in the melt in preferably less than about 250 micron, more preferably less than about 100 micron. In preferred embodiments, the melt is dispensed from the nip of a pair of counter-rotating, heated rollers having a nip setting of less than about 400 microns, preferably from about 150 to about 300 microns, the substrate being arranged for movement counter to one of the rollers and in contact therewith, whereby the melt is transferred to the substrate by a wiping action. Thereafter, the substrate

passes through smoothing and distributing means, for example a pair of plates stationed on opposite sides of the substrate at a spacing of less than about 300 microns, preferably from about 120 to about 220 microns. Finally, the coated substrate is cooled in a current of air.

The invention is illustrated in the following non-limitative Examples in which parts and percentages are by weight unless otherwise specified.

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

LAS	:	Linear C_{12} alkyl benzene sulphonate
$C_{12/14}AS$	:	Sodium C_{12}-C_{14} alkyl sulphate
TAE_n	:	Hardened tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol
$C_{12}TMAB$	:	C_{12} alkyl trimethyl ammonium bromide
Dobanol 45-E-7	:	A C_{14}-C_{15} primary alcohol condensed with 7 moles of ethylene oxide, marketed by Shell
PEG	:	Polyethylene glycol (MWt normally follows)
TAED	:	Tetraacetylethylenediamine
PAG	:	Pentaacetylglucose
AOBS	:	Sodium p-acetoxy benzene sulphonate
Silicone/Silica	:	85% polydimethyl siloxane 15% silanated silica
Porphine	:	Tri/tetra sulphonated zinc phthalocyanine
Gantrez AN119	:	Maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of 240,000, marketed by GAF. This material was prehydrolysed with NaOH before addition.

Perborate	:	Anhydrous sodium perborate bleach of empirical formula $NaBO_2.H_2O_2$
EDTA	:	Sodiumethylenediaminetetraacetate
Brightener 1	:	Disodium 4,4'-bis(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2:2'-disulphonate
Brightener 2	:	Disodium 4,4'-bis(2;sulphonato styryl)biphenyl
DETPMP	:	Diethylenetriamine penta(methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
EDTMP	:	Ethylenediamine tetra(methylene phosphonic acid), marketed by Monsanto, under the Trade name Dequest 2041
Substrate 1	:	Non-woven fabric formed of 100% unbleached crimped rayon fibres of 1.5 denier bonded with 23% polyacylate binder; basis weight 35 g/m^2; 17 elliptical apertures/cm^2; aperture width 0.9mm; aperture length 2.5mm
Substrate 2	:	Non-woven fabric formed of 100% unbleached crimped rayon fibres of 1.5 denier bonded with 18% polyacylate binder; basis weight 35g/m^2; 22 square-shaped apertures/cm^2; side dimension 1.1mm

EXAMPLES 1 to 6

Laundry additive products according to the invention are prepared as follows. For each product, the components of the laundry additive composition are mixed at a temperature of about 65°C and passed through a Fryma Colloid Mill, Model MK95-R/MZ 80R (made by M.M. Process Equipment Ltd of M.M. House, Frogmore Road, Hemel Hempstead, Hertfordshire, United Kingdom) in which the grinding faces are set to a separation of about 180

microns. The melt is then fed through a pair of counterrotating rolls heated to 76°C and having a nip setting of 250 microns and is transferred to substrate moving counter to one of the rollers by wiping. The coated substrate is finally passed between a pair of static plates having a spacing of 180 microns, air-cooled, and cut into sheets of size 35 X 23cm.

	EXAMPLES					
	1	2	3	4	5	6
LAS	-	3	-	-	5	-
$C_{12/14}AS$	5	3	6	3	3	8
TAE_{25}	-	3	-	-	-	4
$C_{12}TMAB$	2	-	4	3	-	3
Dobanol 45E7	5	3	5	4	5	-
PEG 8000	5	5	7	6	7	8
TAED	5	-	-	-	-	-
PAG	-	3	-	-	3	-
AOBS	-	-	-	1	-	-
Silicone/Silica	0.3	0.2	0.2	0.2	0.3	0.3
Porphine	-	0.2	-	-	-	0.3
Gantrez AN119	0.3	-	-	0.8	-	0.5
Perborate	-	-	-	5	-	-
EDTA	-	-	-	0.2	-	-
Brightener 1	-	0.3	0.1	-	0.2	0.1
Brightener 2	0.1	0.1	-	0.2	-	0.3
DETPMP	0.5	1	-	-	0.8	1
EDTMP	-	-	1.5	0.5	-	-
Moisture	0.8	0.5	0.6	0.2	0.5	0.7
Substrate 1	2.8	2.8	-	2.8	-	-
Substrate 2	-	-	2.8	-	2.8	2.8
Percent Coated Apertures	40	33	45	50	42	55

The above products are effective laundry detergents combining a high composition:substrate ratio with excellent flexibility, product release, feel and storage characteristics.

CLAIMS

1. A laundry additive product characterized by

(a) a solid laundry additive composition having a softening temperature of at least 35°C and comprising at least 40% of a water-soluble or water-dispersible matrix of organic materials having a melting completion temperature of less than 85°C, and

(b) a flexible, sheet-like apertured substrate having an aperture density of from 10 to 30 apertures per sq cm of sheet and wherein the apertures, on average, have a width of from 0.5mm to 5mm and a length of from 0.8mm to 5mm, the substrate carrying a water releasable coating of the laundry additive composition and having areas of uncoated apertures and areas wherein the coating covers the apertures and extends between opposing surfaces of the substrate, the ratio of areas of uncoated to coated apertures being in the range from 15:1 to 1:3 and wherein the weight ratio of composition:substrate is at least 5:1.

2. A product according to Claim 1 characterized in that the substrate has an aperture density of from about 13 to about 26, preferably from about 16 to about 23 apertures per sq cm of sheet.

3. A product according to Claim 1 or 2 characterized in that the apertures, on average, have an area of from about 0.7 to about 7mm^2 and a ratio of length:width of from 1:1 to about 6:1, preferably from 1:1 to about 4:1.

4. A product according to any of Claims 1 to 3 characterized in that the apertures are elongate having, on average, a width of from about 0.8mm to about 1.5mm and a length of from about 2mm to about 3.5mm, or are generally square-shaped with a side dimension of from about 1mm to about 2.5mm.

5. A product according to any of Claims 1 to 4 characterized in that the substrate has a basis weight of from about 10 to about 70 grams/sq. metre and a hydrophobic binder resins content of from about 12% to about 25%, preferably from about 16% to about 22%.

6. A product according to any of Claims 1 to 5 characterized by at least about 50%, preferably at least about 60%, of organic matrix materials having a melting completion temperature of less than about 75°C, preferably less than about 70°C, wherein the laundry additive composition has a softening temperature of at least about 40°C, preferably at least about 50°C.

7. A product according to any of Claims 1 to 6 characterized in that the weight ratio of composition: substrate is at least about 6:1, preferably at least about 7:1, and wherein the ratio of the areas of uncoated to coated apertures is from about 6:1 to about 1:2, preferably from about 4:1 to about 1:1.

8. A product according to any of Claims 1 to 7 characterized by at least 5%, preferably at least 15% of water-soluble or water-dispersible organic binding agent having a melting onset temperature of at least about 35°C and a melting completion temperature of less than about 85°C.

9. A product according to Claim 8 characterized in that the binding agent is selected from polyethylene glycols of molecular weight greater than about 1000, C_{12}-C_{18} fatty

acids and esters and amides thereof, polyvinyl pyrrolidone of molecular weight in the range from about 40,000 to about 700,000, and C_{14}-C_{24} fatty alcohols ethoxylated with from about 14 to about 100 moles of ethylene oxide.

10. A product according to Claim 8 or 9 characterized in that the binding agent comprises at least about 40%, preferably at least about 50% thereof of polyethylene glycol having a molecular weight greater than about 4,000.

11. A product according to any of Claims 1 to 10 characterized by at least about 5%, preferably at least about 20%, of organic detergent selected from anionic, nonionic and cationic surfactants and mixtures thereof.

12. A product according to any of Claims 1 to 11 characterized by at least about 5% of an inorganic or organic peroxy bleach and/or at least 2% of an organic peroxy acid bleach precursor.

European Patent Office

EUROPEAN SEARCH REPORT

0096566
Application number
EP 83 30 3237

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	US-A-3 930 086 (C. HARMON) * Claim 1 *		C 11 D 17/04
D,A	US-A-4 170 565 (D.J. FLESHER et al.) * Claim 1 *		
A	GB-A-1 392 994 (NOVIPRO) * Claim 1 *		
A	DE-A-2 744 642 (PROCTER & GAMBLE CO.) * Claims 1, 5, 6, 17, 25, 30 *		
P,A	EP-A-0 075 987 (PROCTER & GAMBLE EUROPEAN TECHNICAL CENTER) * Claims 1, 4, 5 *		

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 11 D 17/00
D 04 H 1/00
D 06 F 39/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	23-08-1983	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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