

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 October 2003 (23.10.2003)

PCT

(10) International Publication Number
WO 03/087285 A1

- (51) International Patent Classification⁷: **C11D 11/00**, 1/835
- (21) International Application Number: PCT/EP03/02700
- (22) International Filing Date: 14 March 2003 (14.03.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0208696.5 16 April 2002 (16.04.2002) GB
- (71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, OM, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).
- (71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).
- (71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, 400 020 Mumbai (IN).
- (72) Inventors: **FRY, Alan, John**; 35 Winchester Avenue, Ellesmere Port, Cheshire CH65 5DL (GB). **MOHAMMADI, Mansur, Sultan**; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).
- (74) Agents: **ELLIOTT, Peter, William** et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FABRIC TREATMENT COMPOSITION

(57) Abstract: A heat activated fabric treatment composition comprises from 3 to 75wt% of one or more fabric treatment active ingredients, from 5 to 60wt% of a nonionic surfactant and from 10 to 50 wt% of water. The composition is provided in a dispensing device which, in use, is attached to the internal panel of a tumble dryer.

WO 03/087285 A1

FABRIC TREATMENT COMPOSITION

Field of the Invention

The present invention relates to a fabric treatment composition. The invention particularly relates to a heat activated fabric treatment composition for use in a tumble dryer.

Background of the Invention

In the treatment of fabrics in a tumble dryer it is known to add one or more conditioning agents together with the load to be dried. For instance, for imparting a softening benefit to fabrics it is known from CA 1,005,204 to co-mingle fabrics in a tumble dryer with a flexible substrate carrying a normally solid fabric conditioning agent. In co-mingling fabrics with impregnated substrates, however, there is a risk that the conditioner may not be evenly distributed. Furthermore, the co-mingling of the fabrics with impregnated substrates requires the separation of the substrate from the fabrics after the completion of the tumble dryer treatment. This separation is often time-consuming in that the substrates cannot readily be located.

Other disadvantages of such products include uneven product distribution following entanglement of the substrate with fabrics which can lead to greasy marks on fabrics (staining) and the tendency of such substrates to become positioned over the tumble dryer vent, thus giving virtually no benefit

- 2 -

to the fabrics during a tumble drying cycle. Furthermore, these products are designed for single use only and therefore need to be replaced after every cycle. In addition, perfume delivery from the substrate onto fabrics is often poor resulting in consumers using additional substrates to deliver adequate perfume which is wasteful of resources.

For overcoming these problems it has been suggested, for instance in GB 2,066,309 and US 3,634,947, to use conditioner dispensing articles, comprising means for attachment of the substrate to the tumble dryer wall. Other proposals, such as for instance disclosed in GB 1,399,728, involve the use of separate means for attaching the conditioning article to the tumble dryer wall.

EP-B-361593 concerns an alternative approach in which a fabric conditioning article comprises a combination of a substrate and a fabric conditioning composition, the substrate being a porous material with a specified void volume and cell count. The article of EP-B-361593 is designed to adhere to the tumble dryer wall.

US 4053992 discloses a hemispherical device that fits onto the door of a tumble dryer and delivers fabric conditioner from sheets.

US 5787606 discloses a dispenser on the door of a tumble dryer containing a roll of tumble dryer sheets.

- 3 -

WO-A-97/42290 discloses solid compositions that can be delivered by any convenient applicator fixed to the door or to the surface of the drum of the tumble dryer.

US 5040311 discloses a device for inside a tumble dryer for delivering a conventional aqueous fabric conditioner where the fabric conditioner migrates outwardly to the surface of the device to become engaged with clothes because of the heat and tumbling in the dryer. Staining from such liquid fabric conditioners that "wet" fabrics is mentioned.

US 5966831 discloses a foam carrier for the inside of a tumble dryer impregnated with microencapsulated fluid where the microcapsules rupture because of mechanical and heat action.

US 4642908 discloses a valve-containing device attached to the non-rotating head of a tumble dryer drum for delivering accurate and metered amounts of a fluid.

US 4014105 discloses a device with multiple openings for the inside of a tumble dryer. Aqueous liquid conditioners are referred to, but the product is permanently in a liquid state and thus does not address the problem of leakage from the dispensing device during storage.

WO-A1-00/58428 discloses a heat activated cleaning composition for dry-cleaning of textiles and garments.

WO-A1-97/26316 relates to tumble dryer articles comprising a mixture of nonionic and anionic surfactants. EP-A2-0539025 discloses fragrance microcapsules for fabric conditioning.

- 4 -

The microcapsules are spray dried and incorporated into a tumble dryer article.

In our co-pending applications, WO-A1-02/33160 and WO-A1-02/33161, there are disclosed articles suitable for treatment fabrics in a tumble dryer. The compositions of the present invention are particularly suitable for use with such devices.

In order to optimise the delivery of the active material onto fabrics during the drying cycle, it is desirable to provide a fabric treatment composition which, at a temperature below the heating cycle temperature of the tumble dryer, remains substantially within a dispensing article and is capable of undergoing a transition during the heating cycle of a tumble dryer such that it can be dispensed from the dispensing article

It is, therefore, desirable to provide a fabric treatment composition which is capable of undergoing such transitions without unacceptable instability. It is particularly desirable that the composition can undergo such a cycle repeatedly.

US 4014432 relates to a product for fabrics treatment in tumble drying machines. Disclosure is made of conditioning agents which are normally solid at room temperature and soften sufficiently at the tumble dryer operating temperature to be exuded through perforations within the product. The conditioning agent is preferably a quaternary ammonium fabric softening agent in admixture with a nonionic

- 5 -

surfactant. A very brief reference is made to aqueous solutions or dispersions and, in the examples, compositions comprising either a 1.8% aqueous solution of 3-alkoxyloxy-2-hydroxypropyl trimethyl ammonium chloride or a 4.8% aqueous solution of lauryl dimethyl ammonio propane sulphonate are disclosed. There is no reference to the consumer perceivable problem of staining.

Effective delivery of a fabric treatment composition from a device such as described above requires the composition to be flowable at the delivery temperature (i.e. the heating temperature of the tumble dryer). The inventors have identified a problem with fabric treatment compositions which are suitable to be delivered onto fabrics in a liquid state in that they can leave stain marks on the treated fabric.

Fabric staining is referred to in US 5066413, US 4049858, WO-A-97/42290 and US4149977. However, this is in relation to tumble dryer sheet conditioning compositions only.

The problem of staining is particularly associated with distributing a substantially liquid product during the heating cycle of a domestic tumble dryer. For this reason, liquid fabric treatment compositions are usually delivered in a washing machine rinse cycle and not in a tumble dryer heating cycle.

Without wishing to be bound by theory, the applicants believe that the visibility of such stains originates from the reduction in the reflection of light from the surface of

- 6 -

the stained fabric compared to the reflection from adjacent unstained part of the fabric. More particularly, the visibility of the stain is due to the difference in the refractive index of the fibre of the fabric and that of the composition delivered.

It is also believed that the level of staining is affected by whether the delivered composition fills the spaces between fibres or spreads on the fibres themselves. The stain becomes more visible if the air between the fibres is replaced with the composition since this reduces the difference in refractive index between the fibre and the surrounding fabric giving rise to more transmitted light and less reflection.

The visibility of a stain is also believed to be affected by the thickness and evenness of spreading of the composition onto fabrics. Thin, even spreading of the composition is most desirable and thus viscosity and surface tension characteristics of the fabric treatment composition which improve thin, even spreading are particularly desirable.

Nevertheless, a composition which is delivered as a liquid onto fabrics is desirable since it is believed that a liquid will be dispensed and distributed evenly during delivery.

Accordingly, it is desirable to provide a heat activated fabric treatment composition which can be delivered as a liquid during the heating cycle of a tumble dryer from a dispensing device and which addresses the problem of staining.

- 7 -

Furthermore, it is desirable to provide a heat activated fabric treatment composition which delivers anti-static benefits. Additionally, it is desirable to provide good perfume longevity and/or perfume substantivity to fabrics treated using the compositions of the invention.

It is further desirable to provide a heat activated fabric treatment composition which can be stored in a dispensing device and which can undergo repeated cycles from a more viscous storage state to a less viscous dispensable state such that during the heating cycle of the tumble dryer at least part of the composition is delivered to fabrics.

Objects of the Invention

The present invention seeks to address one or more of the abovementioned problems and to provide one or more of the abovementioned benefits.

Statement of Invention

Thus, according to the present invention there is provided a heat activated fabric treatment composition comprising:

- (a) from 3 to 75wt% of one or more fabric treatment active ingredients;
- (b) from 5 to 60 wt% of a nonionic surfactant; and
- (c) from 10 to 50 wt% of water

- 8 -

According to a further aspect of the invention, there is provided a package comprising a composition as defined above within a dispensing device.

The invention further provides a method of conditioning fabrics in a tumble dryer comprising providing the heat activated fabric treatment composition in a dispensing device, locating the dispensing device on the internal panel of the door of the tumble dryer, inserting fabrics into the tumble dryer and operating the dryer to cause at least a part of the fabric treatment composition to be dispensed from the device onto the fabrics being dried so as to condition the fabrics.

Detailed Description of the Invention

In the context of the present invention, "heat activated" means that composition is suitable for use in a domestic tumble dryer, and preferably means that the composition is substantially solid at ambient temperature, i.e. 20°C, and undergoes a transition to a substantially liquid state at the heating temperature of a domestic tumble dryer.

Since the heating temperature of a domestic tumble dryer is typically within the range from about 40°C to about 80°C, it is particularly preferred that the composition is substantially solid at temperatures below 30°C, more preferably below 32°C, most preferably below 35°C, e.g. below 37°C and is substantially liquid, or at least mobile,

- 9 -

at temperatures above 45°C, more preferably above 40°C, most preferably above 37°C. It is desirable that the composition is fully melted at temperatures above 50°C.

According to one method of defining the temperature at which the composition flows, it is desirable that the slip point of the composition is greater than 30°C and less than 50°C, more preferably greater than 35°C and less than 47°C, most preferably greater than 37°C and less than 45°C.

The slip point of the composition is measured as defined by British Standard BS 684 section 1.3 1991 ISO 6321:1991 (UK).

Product Form

In order to provide a fabric treatment composition capable of remaining substantially within a dispensing device during storage and being delivered to fabrics during the heating cycle of a tumble dryer, it is important that the composition has viscosity characteristics which allow the transition from a storage state to a dispensing state to occur at or about the heating temperature of the heat cycle. That is, the composition should preferably be a non-flowing, high viscosity product at ambient temperatures, e.g. a solid, soft solid or gel, and should become a low viscosity product, e.g. a liquid, at the heating temperatures of the tumble dryer.

- 10 -

Most preferably the composition is a "gel" at ambient temperature comprising a crystalline state forming a network to give the composition a non-flowing gel or gel-like consistency. At the heating temperature of the tumble dryer, the composition is most preferably a "sol" comprising a clear or isotropic solution.

Ideally, at the heating temperature the composition is a single phase or, if multi-phasic, the dispersed phase has unit sizes smaller than a typical membrane pore size of a dispensing device. A typical membrane has a pore size in the range of 0.1 - 10 microns. For pore sizes much smaller than this dispensing becomes difficult whilst for much larger pore sizes, too much composition is released per cycle, thereby increasing the risk of staining.

Typically the composition will have a viscosity of above 375 mPa.s at a shear rate of 100s^{-1} at ambient temperature, more preferably above 450 mPa.s, most preferably above 500 mPa.s, e.g. above 600 mPa.s. The viscosity of the composition at ambient temperature can be measured by first melting the composition (if necessary), transferring it to a viscometer cup and then letting it cool to room temperature with gentle shearing.

At the heating temperature of a domestic tumble dryer, the composition will typically have a viscosity of below 350 mPa.s at 100s^{-1} , more preferably below 300 mPa.s, most preferably below 250 mPa.s, e.g. below 200 mPa.s.

- 11 -

Measurements can be made using a Haake Rotoviscometer RV20 cup and bob NV1.

In order to provide optimal anti-staining benefits together with improved delivery of the composition to fabrics and better cycling between the storage state and dispensing state, the carrier system for the active ingredient(s) preferably comprises a nonionic surfactant, water and optionally a solvent.

Nonionic surfactant

The nonionic surfactant is present in order to improve control of the melting temperature of the composition or at least to affect the temperature at which the composition flows.

Preferred nonionic surfactants are solid at ambient temperature so that, once deposited onto fabrics, they cause greater scattering light from the fabrics thereby reducing visibility of any product deposited onto the fabric.

Furthermore, the preferred nonionic surfactants have an HLB within the range 8 to 20, more preferably 10 to 20, as this significantly improves solubilisation of the active components (such as fabric softening agents which typically have a solubility of less than 1×10^{-3} wt% in water at 20°C) in the water phase at the elevated temperatures of the heating cycle.

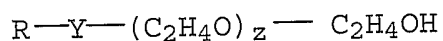
- 12 -

Suitable nonionic surfactants include addition products of ethylene oxide and/or propylene oxide with fatty alcohols, fatty acids and fatty amines.

Ideally, the nonionic surfactant comprises an average degree of alkoxylation of from 8 to 40 alkoxy units per molecule, more preferably 10 to 30, even more preferably 11 to 25, e.g. 12 to 22 alkoxy units.

Any of the alkoxyated materials of the particular type described hereinafter can be used as the nonionic surfactant.

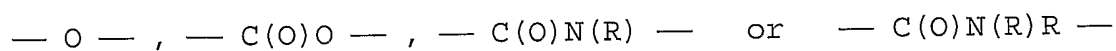
Suitable surfactants are substantially water soluble surfactants of the general formula:



where R is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups; primary, secondary and branched chain alkenyl hydrocarbyl groups; and primary, secondary and branched chain alkenyl-substituted phenolic hydrocarbyl groups; the hydrocarbyl groups having a chain length of from 8 to about 25, preferably 10 to 20, e.g. 14 to 18 carbon atoms with coco and tallow or chain composition being most preferred.

In the general formula for the ethoxylated nonionic surfactant, Y is typically:

- 13 -



in which R has the meaning given above or can be hydrogen;
and Z is preferably from 8 to 40, more preferably from 10 to 30, most preferably from 11 to 25, e.g. 12 to 22.

The degree of alkoxylation, Z denotes the average number of alkoxy groups per molecule.

Examples of nonionic surfactants follow. In the examples, the integer defines the number of ethoxy (EO) groups in the molecule.

A. Straight-Chain, Primary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, and pentadecaethoxylates of n-hexadecanol, and n-octadecanol having an HLB within the range recited herein are useful viscosity/dispersibility modifiers in the context of this invention. The ethoxylates of mixed natural or synthetic alcohols in the "tallow" chain length range are also useful herein. Specific examples of such materials include tallow alcohol-EO(11), tallow alcohol-EO(18), and tallow alcohol-EO(25), coco alcohol-EO(10), coco alcohol-EO(15), coco alcohol-EO(20) and coco alcohol-EO(25).

B. Straight-Chain, Secondary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, pentadeca-, octadeca-, and nonadeca-ethoxylates of 3-hexadecanol, 2-

- 14 -

octadecanol, 4-eicosanol, and 5-eicosanol having an HLB within the range recited herein are useful viscosity and/or dispersibility modifiers in the context of this invention. Exemplary ethoxylated secondary alcohols useful herein as the viscosity and/or dispersibility modifiers of the compositions are: C₁₆ EO(11); C₂₀ EO(11); and C₁₆ EO(14).

C. Alkyl Phenol Alkoxyates

As in the case of the alcohol alkoxyates, the hexa- to octadeca-ethoxyates of alkylated phenols, particularly monohydric alkylphenols, having an HLB within the range recited herein are useful as the viscosity and/or dispersibility modifiers of the instant compositions. The hexa- to octadeca-ethoxyates of p-tri-decylphenol, m-pentadecylphenol, and the like, are useful herein. Exemplary ethoxylated alkylphenols useful as the viscosity and/or dispersibility modifiers of the mixtures herein are: p-tridecylphenol EO(11) and p-pentadecylphenol EO(18).

As used herein and as generally recognized in the art, a phenylene group in the nonionic formula is the equivalent of an alkylene group containing from 2 to 4 carbon atoms. For present purposes, nonionics containing a phenylene group are considered to contain an equivalent number of carbon atoms calculated as the sum of the carbon atoms in the alkyl group plus about 3.3 carbon atoms for each phenylene group.

- 15 -

Phenolic alkoxyates are particularly preferred because they are believed to provide improved anti-static benefits on fabrics treated in a tumble dryer.

D. Olefinic Alkoxyates

The alkenyl alcohols, both primary and secondary, and alkenyl phenols corresponding to those disclosed immediately herein above can be ethoxylated to an HLB within the range recited herein and used as the viscosity and/or dispersibility modifiers of the instant compositions.

Olefinic alkoxyates are preferred for the same reason as phenolic alkoxyates.

E. Branched Chain Alkoxyates

Branched chain primary and secondary alcohols which are available from the well-known "OXO" process can be ethoxylated and employed as the viscosity and/or dispersibility modifiers of compositions herein.

Although branched chain alkoxyates and secondary alkoxyates are within the scope of the invention, it is most preferred that any alkoxyated nonionic surfactant is an alkoxyated straight chain primary alcohol.

F. Polyol Based Surfactants

Suitable polyol based surfactants include sucrose esters such sucrose monooleates, sucrose monostearate or mixture

- 16 -

thereof, poly glycerols, alkyl polyglucosides such as coco or stearyl monoglucosides and stearyl triglucoside and alkyl polyglycerols.

The above nonionic surfactants are useful in the present compositions alone or in combination, and the term "nonionic surfactant" encompasses mixed nonionic surface active agents.

Sucrose based surfactants are highly suitable because of their higher hydration state relative to other alkoxykates.

The nonionic surfactant is present in an amount within the range from 5 to 60% by weight based on the total weight of the composition, more preferably from 10 to 50wt%, most preferably from 15 to 45wt%.

Water

The compositions of the invention comprise water and are preferably aqueous.

The water-based nature of the compositions of the present invention is believed to help reduce staining and is unlike conventional tumble dryer sheets which are substantially non-aqueous.

Water is present at a level of from 10 to 50%, preferably from 15 to 40%, more preferably from 20 to 35% by weight based on the total weight of the composition.

- 17 -

When deposited onto fibre during the drying cycle, any water is preferably present as a continuous phase which may partially evaporate and/or remain partially associated with the active ingredient(s).

An unexpected benefit of water-based compositions is that the amount of staining is less dependent on the amount of delivery of the composition per heating cycle of the tumble dryer. This is advantageous over prior art systems such as disclosed in US 4149977, which typically must rely on maintaining full control over the amount of composition delivered in each cycle to control staining.

It is believed that the nonionic surfactant and fabric treatment active ingredient are solubilised into the aqueous phase at the heating temperature of the tumble dryer so that the aqueous phase acts as a carrier for depositing the fabric treatment active onto fabrics. During heating, the water is then evaporated leaving the deposited fabric treatment active.

Solvent

Optionally and advantageously, the compositions comprise a solvent for the active ingredient(s). The solvent further optimises the viscosity and flow temperature characteristics of the composition. Additionally, the solvent may act as a humectant retarding the loss of water from the composition upon storage.

Preferably the solvent is semi-polar.

- 18 -

Suitable solvents include any which have a flash point above the heating temperature of a tumble dryer. Ideally the solvent is also odourless.

Commercially available examples include polyols. Particularly preferred are glycol-based solvents such as glycol ethers. The most preferred solvent is dipropylene glycol.

The solvent is preferably present at a level of from 1 to 25%, more preferably from 2 to 20%, most preferably from 3 to 10% by weight, based on the total weight of the composition.

Preferably the weight ratio of nonionic surfactant to solvent is from 1:1 to 15:1, more preferably from 3:2 to 8:1 most preferably from 2:1 to 6:1.

The combined amount of nonionic surfactant and optional solvent is preferably less than 50% by weight of the composition, more preferably less than 47%, most preferably less than 45%.

Fabric Treatment Active Ingredient

Any active ingredient typically delivered in the rinse cycle of a laundry operation or in a tumble drying cycle is suitable for use in the compositions of the present invention.

- 19 -

The nonionic surfactant is preferably present in an amount greater than the fabric treatment active ingredient.

Preferably the nonionic surfactant is present in a weight excess, more preferably in a molar excess relative to the fabric treatment active ingredient.

Ideally, the molar ratio of fabric treatment active ingredient to nonionic surfactant is within the range from 2:1 to 1:25, more preferably from 1:1 to 1:15 most preferably from 1:1 to 1:7, e.g. 2:3 to 1:5.

Preferably the weight ratio of fabric treatment active ingredient to nonionic surfactant is within the range from 2:1 to 1:100, more preferably from 3:2 to 1:75, most preferably from 1:1 to 1:20, e.g. 2:3 to 1:5.

The following are examples of suitable active ingredients. The list is not exhaustive and it will be appreciated by the person skilled in the art that further active ingredients are equally suitable for use in the compositions of the present invention.

Antistatic Agents

Suitable antistatic agents include humectants, such as glycerol and potassium acetate, inorganic salts, such as lithium chloride, and amines, such as triethanolamine. Ionising antistatic agents are believed to be more efficient than non-ionic antistatic agents, and thus it is desirable that the agent is sufficiently hygroscopic to form a

- 20 -

solution in equilibrium with atmosphere below 40% relative humidity.

Especially preferred antistatic agent include NH_4 DEFI/fatty acid systems containing up to 80% fatty acid, 25/75 LAS/Fatty acid systems, quaternary ammonium compounds where one or more of the alkyl groups is substituted by a poly(oxyethylene) group, perquaternised alkylene-diamine derivatives, polyamines containing poly(oxyethylene) groups, PEG 600, combinations of non-ionic and cationic surfactants as described in US 4058489 preferably with both surfactants being covalently bound, combinations of a quaternary ammonium material and a non-ionic surfactant as described in Textile Month May 1983, 22, tri-methyl benzyl ammonium chloride, tri-octyl ammonium chloride, tri-methyl benzyl ammonium chloride, Gafstat S100 (ex Gaf Corp.), Alubrasol MM (ex Jordan Chem. Co.), tetrabutyl ammonium bromide preferably in combination with di-octyl dimethyl ammonium bromide, combinations of quaternary ammonium materials and magnesium or calcium salts (CaCl_2 , CaSO_4 , MgSO_4) as described in US 3951879, mixtures of mono- and di-substituted alkanediamines, produced by reaction of higher alkyl-1,2-epoxides with lower alkanediamines as described in US 4049557, N-substituted iminodicarboxylates as described in US 3725473, alkyl ammonium carbamates of the form $\text{R}_1\text{R}_2\text{NH}_2^+\text{O}(\text{O})\text{CNR}_3\text{R}_4$, where R_1 is hydrogen or an alkyl group, e.g. 1 to 22 atoms; R_2 is an alkyl group having 10 or more carbon atoms (preferably 10 to 22); R_3 and R_4 are each either hydrogen or an alkyl group (1 to 22 carbons) as described in US 3962100, polyalkylethyleneimine of the form

- 21 -

-[N(R')(CH₂)_y]_z- where y is an integer from 1 to 4, preferably 2, z is an integer greater than 1, preferably 20 to 10000, R' is selected from the group consisting of hydrogen, and alkyl and alkanoyl substituents containing preferably from 12 to 18 carbon atoms and preferably 10 to 20% of the nitrogen atoms are substituted with alkyl and alkanoyl substituents as described in US 3844952, mono- or di- long chain alkyl imidazolinium compounds as described in US 3959157, mixtures of nonionic, cationic and anionic surfactants as described in US 4058489

Fabric Softening Agents

Suitable fabric softening agents include cationic surfactants such as quaternary ammonium fabric softening materials and imidazolines as well as nonionic fabric softening agents.

When the fabric treatment active ingredient comprises a cationic surfactant, it is preferred that a nonionic surfactant is present. The nonionic surfactant co-micellises the cationic surfactant thereby increasing dissolution of the active ingredient into the aqueous phase. This provides excellent transfer of ingredients through the membrane pores and increases the liquidity of the activated composition, thereby improving deposition onto fabrics.

If the fabric softening agent is a quaternary ammonium fabric softening material, it preferably has two C₁₂₋₂₈ alkyl or alkenyl groups connected to the nitrogen head group,

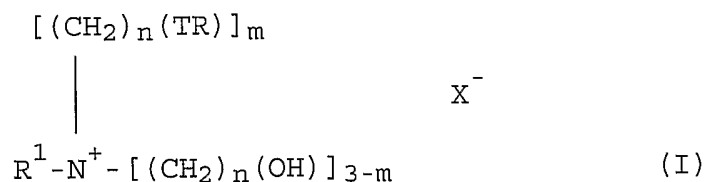
- 22 -

preferably via at least one ester link. It is more preferred if the quaternary ammonium material has two ester links present.

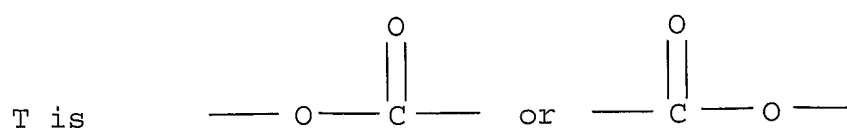
Preferably, the average chain length of the alkyl or alkenyl group is at least C₁₄, more preferably at least C₁₆. Most preferably at least half of the chains have a length of C₁₈.

It is generally preferred that the alkyl or alkenyl chains are predominantly linear.

The first group of cationic fabric softening compounds for use in the invention is represented by formula (I):



wherein each R is independently selected from a C₅₋₃₅ alkyl or alkenyl group, R¹ represents a C₁₋₄ alkyl, C₂₋₄ alkenyl or a C₁₋₄ hydroxyalkyl group,



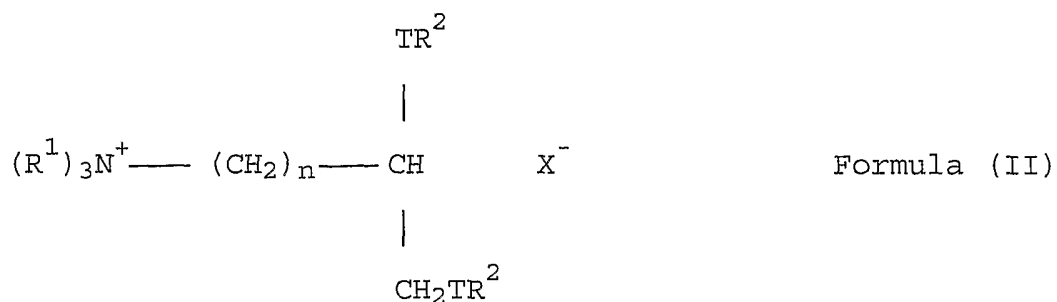
n is 0 or a number selected from 1 to 4, m is 1, 2 or 3 and denotes the number of moieties to which it relates that pend

- 23 -

directly from the N atom, and X^- is an anionic group, such as halides or alkyl sulphates, e.g. chloride, methyl sulphate or ethyl sulphate.

Especially preferred materials of this class are di-alkenyl esters of triethanol ammonium methyl sulphate. Commercial examples include Tetranyl AHT-1 (di-hardened oleic ester of triethanol ammonium methyl sulphate 80% active), AT-1 (di-oleic ester of triethanol ammonium methyl sulphate 90% active), L5/90 (palm ester of triethanol ammonium methyl sulphate 90% active), all ex Kao, Rewoquat WE15 (C_{10} - C_{20} and C_{16} - C_{18} unsaturated fatty acid reaction products with triethanolamine dimethyl sulphate quaternised 90 % active), ex Witco Corporation.

The second group of cationic fabric softening compounds for use in the invention is represented by formula (II):

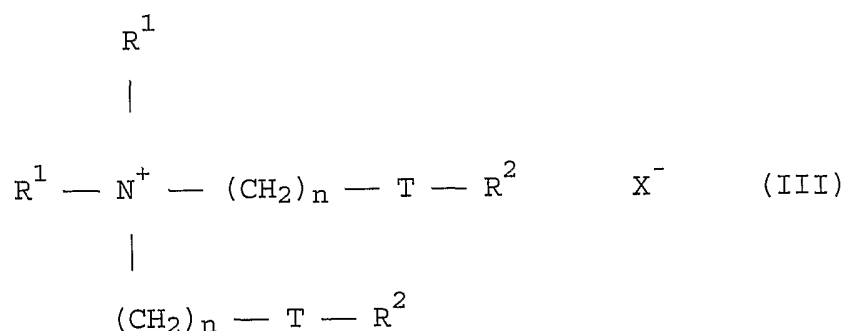


wherein each R^1 group is independently selected from C_{1-4} alkyl, hydroxyalkyl or C_{2-4} alkenyl groups; and wherein each R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups; n is 0 or an integer from 1 to 5 and T and X^- are as defined above.

- 24 -

Preferred materials of this class such as 1,2 bis[tallowoyloxy]-3- trimethylammonium propane chloride and 1,2-bis[oleyloxy]-3-trimethylammonium propane chloride and their method of preparation are, for example, described in US 4137180 (Lever Brothers), the contents of which are incorporated herein. Preferably these materials also comprise small amounts of the corresponding monoester, as described in US 4137180.

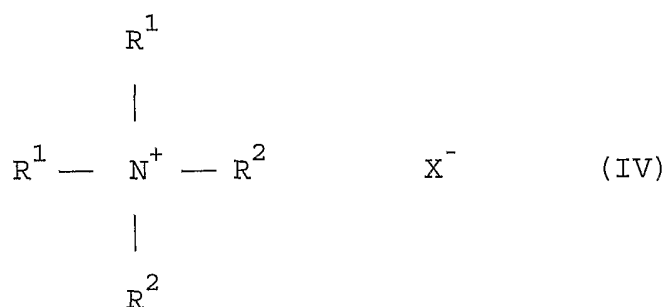
A third group of cationic fabric softening compounds for use in the invention is represented by formula (III):



wherein each R^1 group is independently selected from C_{1-4} alkyl, or C_{2-4} alkenyl groups; and wherein each R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups; n is 0 or an integer from 1 to 5 and T and X^- are as defined above. A preferred material of this class is N,N-di(tallowoyloxyethyl)-N,N-dimethyl ammonium chloride.

- 25 -

A fourth group of cationic fabric softening compounds for use in the invention is represented by formula (IV):



wherein each R^1 group is independently selected from C_{1-4} alkyl, or C_{2-4} alkenyl groups; and wherein each R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups; and X^- is as defined above.

It should also be appreciated that certain fabric softening agents may also deliver anti-static benefits to fabrics.

For instance, quaternary ammonium materials with one or more alkoxyate groups per molecule are believed to deliver both good softening and good antistatic to fabrics.

Fabric softening agents which also deliver anti-static benefits are particularly preferred.

The fabric treatment active ingredient is present in an amount from 3 to 75% by weight (active ingredient) based on the total weight of the composition, preferably 4 to 60% by

- 26 -

weight, more preferably 5 to 50% by weight, most preferably 10 to 45% by weight.

Iodine Value of the Parent Fatty Acyl group or Acid

The iodine value of the parent fatty acyl compound or acid from which the quaternary ammonium fabric softening material is formed is from 0 to 140, more preferably from 0 to 80, most preferably from 0 to 40, e.g. from 0 to 35.

An iodine value below 4 is particularly desirable as the resultant active ingredient provides excellent softening and is more resistant to odour problems upon storage. It is also believed that lower iodine values may reduce staining.

However, iodine values from 5 to 35 are also suitable as the resultant active ingredient melts more readily at the heating temperature of the tumble dryer, and can provide better anti-static benefits.

Where the quaternary ammonium material is based on a parent fatty acid or acyl compound having an iodine value of from 5 to 35, e.g. 10 to 25, it is particularly preferred that the nonionic surfactant comprises a fully saturated alkoxyated alcohol, e.g. hardened tallow 15 EO.

In the context of the present invention, the iodine value of the parent fatty acyl compound or acid from which the fabric softening material formed, is defined as the number of grams of iodine which react with 100 grams of the compound.

- 27 -

The method for calculating the iodine value of a parent fatty acyl compound/acid comprises dissolving a prescribed amount (from 0.1-3g) into about 15ml chloroform. The dissolved parent fatty acyl compound/fatty acid is then reacted with 25 ml of iodine monochloride in acetic acid solution (0.1M). To this, 20ml of 10% potassium iodide solution and about 150 ml deionised water is added. After addition of the halogen has taken place, the excess of iodine monochloride is determined by titration with sodium thiosulphate solution (0.1M) in the presence of a blue starch indicator powder. At the same time a blank is determined with the same quantity of reagents and under the same conditions. The difference between the volume of sodium thiosulphate used in the blank and that used in the reaction with the parent fatty acyl compound or fatty acid enables the iodine value to be calculated.

Perfume

It is desirable that the compositions of the present invention also comprise one or more perfumes. Suitable perfume ingredients include those disclosed in "Perfume and Flavor Chemicals (Aroma Chemicals)", by Steffen Arctander, published by the author in 1969, the contents of which are incorporated herein by reference.

The inventors have found that up to 10wt% perfume can be incorporated in the compositions of the present invention without destabilising the composition. Such levels are significantly higher than those present in commercially available tumble dryer sheets. Accordingly, better perfume

- 28 -

substantivity and longevity can be achieved from the present compositions than from traditional tumble dryer sheets.

Fatty Component

The compositions of the present invention may comprise a fatty component such as a fatty acid and/or a fatty alcohol.

Suitable fatty acids/alcohols have a hydrocarbyl chain length of from 8 to 26 carbon atoms, more preferably 12 to 22, most preferably from 12 to 20 carbon atoms.

Preferred fatty acids include hardened tallow fatty acid (available under the tradename Pristerene, ex Uniqema).

Preferred fatty alcohols include hardened tallow alcohol (available under the tradenames Stenol and Hydrenol, ex Cognis and Laurex CS, ex Albright and Wilson) and behenyl alcohol, a C22 chain alcohol, available as Lanette 22 (ex Henkel).

The fatty acid and/or alcohol is preferably present in an amount of from 0.5% to 15% by weight based on the total weight of the composition. More preferably, the fatty component is present in an amount of from 1 to 10%, most preferably from 1.5 to 7% by weight.

Other co-active ingredients

Other co-active ingredients for the fabric treatment active ingredient may also be incorporated in an amount from 0.01

- 29 -

to 20% by weight, more preferably 0.05 to 10%, based on the total weight of the composition. Preferred ingredients of this type include fatty esters, and fatty N-oxides.

Preferred fatty esters include fatty monoesters, such as glycerol monostearate. If GMS is present, then it is preferred that the level of GMS in the composition, is from 0.01 to 10 wt%, based on the total weight of the composition.

Polymeric viscosity control agents

A polymeric viscosity control agent may also be present in the compositions of the invention. Suitable polymeric viscosity control agents include nonionic and cationic polymers, such as hydrophobically modified cellulose ethers (e.g. Natrosol Plus, ex Hercules) and cationically modified starches (e.g. Softgel BDA and Softgel BD, both ex Avebe). A particularly preferred viscosity control agent is a copolymer of methacrylate and cationic acrylamide available under the tradename Flosoft 200 (ex SNF Floerger).

Polymeric viscosity control agents are preferably present in an amount of from 0.01 to 5wt%, more preferably 0.02 to 4wt%, based on the total weight of the composition.

Other Optional Ingredients

The compositions may also contain one or more optional ingredients conventionally included in fabric conditioning compositions such as pH buffering agents, perfume carriers,

- 30 -

fluorescers, colourants, antifoaming agents, antiredeposition agents, polyelectrolytes, enzymes, optical brightening agents, anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-corrosion agents, drape imparting agents, ironing aids and dyes.

Examples

The invention will now be illustrated by the following non-limiting examples. Further modifications within the scope of the invention will be apparent to the person skilled in the art.

Samples of the invention are represented by a number. Comparative samples are represented by a letter.

All values are % by weight of the active ingredient unless stated otherwise.

The samples in table 1 were prepared as follows:

The quat, nonionic and optional solvent were weighed in a beaker and heated on a hot plate until molten (about 70°C). The molten mixture was then added with stirring to hot water (also about 70°C) to which optional components such as a polyelectrolyte or salt had already been added. To this mixture, perfume was added and stirring continued until a 'clear' liquid was produced. The liquid was bottled and left to cool either in the bottle or on a rotary blender.

Table 1

Sample	A	1	2	3	4	5	6	7
Quat (1) *	80	10	20	0	0	0	0	0
Quat (2) *	0	0	0	40	40	40	30	10
Quaternised triethylene amine (3)	0	0	0	0	0	0	5	0
Polyelectrolyte (4)	0	0	0	0	0	0	0	16
Nonionic surfactant (5)	0	40	40	10	0	15	10	0
Nonionic surfactant (6)	0	0	0	0	15	0	0	33
DPG (7)	10	0	0	0	0	0	15	5
Glycol hydroxy pthalyl hydroxy pthalate (8)	0	0	0	15	10	0	0	0
Water	5	45	35	30	30	40	40	31
Perfume	5	5	5	5	5	5	5	5

(1) Stepanex VL85G(85%), tallow (IV ~ 35) based TEA quaternary ammonium material with 15% DPG solvent (ex Stepan)

(2) Stepanex UL G60 80% (DPG 20%), hardened tallow (IV < 1) based TEA quaternary ammonium material with 20% DPG solvent (ex Stepan)

(3) TEA (ex Aldrich) fully quaternised with di-methyl sulphate

(4) Catiofast CS (30% solution), ex BASF

(5) Genapol C200 (coco alcohol 20EO) ex Clariant

(6) Slovasol 2411, (coco alcohol 11EO) ex Sloveca

(7) dipropylene glycol (ex Dow Chemicals). This was present in addition to any DPG present in the raw material of the quaternary ammonium material.

(8) Glycol HPHP, ex Eastham

For materials in table marked "*", the amount denotes the level of raw material including solvent.

The viscosity of the samples was measured at a shear rate of 106s^{-1} using a Haake Rotoviscometer RV20 cup and bob NV1 at both ambient temperature and at the heating temperature of the tumble dryer. The results are given in table 2.

Table 2

Temp/°C	25	30	32	34	36	38	40	42	44	46	48	50	53	56	58	60	62
A	1067	1040	850	670	510	350	260	190	160	140	120	110	89	77	70	65	65
2	S	S	S	S	S	780	595	231	211	190	173	164	150	133	128	120	105

"S" denotes that the composition was solid.

Delivery Evaluation

Delivery evaluation was carried out as follows:

Approximately 30g of the sample to be evaluated was transferred to a dispensing device - as described on page 16 line 26 to page 20 line 12 and shown in Figures 1, 3 and 4 of WO-A1-02/33161 having a membrane thickness of 160µm, a membrane pore size of 0.2µm and membrane area of 1080mm².

The device was then attached to the inside of the door of a Miele Novotronic T43 tumble dryer and a 60 minute "Cotton Extra Dry" heating cycle started.

For each sample, the amount of product delivered was measured at intervals during the heating cycle. A comparison was also made with commercial tumble dryer sheets. The amount in grams of each sample delivered is given in table 3.

Table 3

Time/mins	0	10	20	30	40	50	60
Temperature/°C	26	47	57	53	34	27	25
Sample A	0	0.03	0.22	0.55	0.77	0.97	1
Sample 2	0	0.09	0.30	0.49	0.85	1.08	1.35
Sample 6	0	0.05	0.25	0.42	0.70	0.95	1.25
Bounce (1)	0	0.2	0.43	0.67	0.8	0.97	0.93
Snuggle (1)	0	0.29	0.46	0.71	0.9	1	1.09

(1) commercial tumble dryer sheets purchased in US December 2001.

Staining Evaluation

Staining evaluation was then carried out on the fabrics identified in Table 4.

Table 4

Garment	Fabric type	Colour	Texture
Single jersey	100% acrylic	Multicolour	Knitted, thick
Sport trousers	100% nylon	Buff	Woven with woven nylon lining, light
Green shirt	100% cotton	Green	Woven, light
Blue shirt	100% Polyester	Blue	Woven peach skin (brushed), heavy
Fleece	52% polyester 40% cotton 8% lastane		Towel looped knit, heavy
Jeans trousers	100% cotton	Blue	Denim
Cotton monitor	100% cotton	Black	Woven, light
Microfibre monitor	100% polyester	Pearly	Woven, light
Pongee monitor	100% polyester	Pink	Tuffata, lining type

A 1.5kg load was washed in a Miele Novotronic W820 washing machine using 80g of un-perfumed Persil fabric washing

- 34 -

powder at a 40°C wash temperature. The fabrics were spin dried and then transferred to a Miele Novotronic T43 tumble dryer.

The dispensing device - as described above - was charged with 30g of the sample and then attached to the internal side of the door of the tumble dryer and the 60 minute "Cotton Extra Dry" drying cycle started. At the end of the cycle the fabrics were removed.

Staining was evaluated by a panel of trained laboratory personnel in a standard Viewing Cabinet (D65 light, simulating typical northern hemisphere outdoor light). The panel assessed the staining of the aqueous compositions with a critical eye using different viewing angles and observing over a black background.

Unless otherwise indicated, each sample was assessed 3 times with the fabric being washed as described above between each assessment.

Staining was ranked according to the number of stains and the size/visibility of the stains on a scale of from 0 to 5 where 0 represented no staining and 5 represented severe staining.

The results are given in table 5 below.

Table 5

Sample	A	1	2	3*	6	7*
Black monitor	2.0-2.0	1.0-1.5	0.5-1.5	1.0-1.5	0.5-1.0	0
Blue shirt	2.0-2.0	0.0-1.5	0.0-1.5	2.0-2.5	0.5-1.5	0
Pongee	3.0-3.0	0.0-1.0	0.0-0.5	1.0-1.5	0.5-1.0	0
Green shirt	1.0-2.0	1.0-1.5	0.0-0.5	1.5-2.0	0-1.5	0
Microfibre (monitor)	1.5-2.0	0.5-1.0	0.0-1.0	2	0.0-2.0	0
Sport trousers	0.0-1.0	0	0	0	0	0
Fleece	0.0-0.50	0	0	0	0	0
Jeans	0.0-0.50	0	0	0	0	0
Jersey	0.0-0.50	0	0	0	0	0

*single test only

Further Staining Evaluation

Staining evaluation was also carried out using the samples (table 1) and a standard commercially available tumble dryer sheet (Bounce, purchased in UK in 2001) over 10 wash and dry cycles.

A 1.5kg load containing equal weight mixtures of cotton, polycotton, polyester, nylon, acrylic, microfibre monitors and pongee polyester monitors was washed as described above. The washed articles were spin dried and transferred to a Hotpoint Aquarius Tumble Dryer and then tumble dried on medium setting for 60 minutes. This process was repeated 10 times, with the dispensing device remaining in position and without being recharged. After each cycle the articles were

- 36 -

removed and assessed then washed and the cycle repeated until 10 cycles completed. For the sample containing the tumble dryer sheet, a new sheet was introduced before each drying cycle.

Staining was evaluated using the method described above. The average results over the ten cycle are given in table 6.

Table 6

Sample	Bounce	2
Delivery/g	0.42	1.15
Pongee	1.13	0.06
Microfibre	1.83	0.39
Average Stain	1.48	0.23

The results demonstrate that the amount of the sample of the invention (and hence the amount of active ingredient) deposited on the fabrics was significantly greater than the amount deposited from the tumble dryer sheet. In spite of this, the staining evaluation results show a significantly lower level of staining on fabrics treated with the sample of the invention than on fabrics treated with the commercially available tumble dryer sheet.

Each sample was evaluated by a trained assessor for static immediately upon removal from the tumble dryer. Evaluation was made on a scale of 0 to 5 where 0 represents no static and 5 represents a very high level of static.

- 37 -

The results are given in the following table.

Table 7

Sample	Bounce	2
Static	2.11	0.11

CLAIMS

1. A heat activated fabric treatment composition comprising:
 - (a) from 3 to 75wt% of one or more fabric treatment active ingredients;
 - (b) from 5 to 60 wt% of a nonionic surfactant; and
 - (c) from 10 to 50 wt% of water
2. A heat activated fabric conditioning composition as claimed in claim 1 wherein the fabric treatment active ingredient is a quaternary ammonium material.
3. A heat activated fabric conditioning composition as claimed in either claim 1 or claim 2 wherein the nonionic surfactant comprises an ethoxylated alcohol having from 12 to 20 EO groups.
4. A heat activated fabric conditioning composition as claimed in any one of the preceding claims wherein the weight ratio of fabric treatment active ingredient to nonionic surfactant is within the range from 2:1 to 1:100.
5. A heat activated fabric conditioning composition as claimed in any one of the preceding claims wherein the weight ratio of fabric treatment active ingredient to

- 39 -

nonionic surfactant is within the range from 3:2 to 1:75.

6. A heat activated fabric conditioning composition as claimed in any one of the preceding claims wherein the weight ratio of fabric treatment active ingredient to nonionic surfactant is within the range from 1:1 to 1:20.
7. A heat activated fabric conditioning composition as claimed in any one of the preceding claims wherein the weight ratio of fabric treatment active ingredient to nonionic surfactant is within the range from 2:3 to 1:5.
8. A heat activated fabric conditioning composition as claimed in any one of the preceding claims comprising a glycol based solvent.
9. A package comprising the heat activated composition of claim 1 within a dispensing device.
10. A method of conditioning fabrics in a tumble dryer comprising locating the package of claim 9 on the internal panel of the door of the tumble dryer, inserting fabrics into the tumble dryer and operating the dryer to cause at least a part of the fabric treatment composition to be dispensed from the device onto the fabrics being dried so as to condition the fabrics.

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/EP 03/02700

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C11D11/00 C11D1/835

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 066 413 A (KELLETT GEORGE W) 19 November 1991 (1991-11-19) cited in the application column 2, line 25 -column 4, line 4 column 5, line 63 -column 6, line 15; examples ----	1-10
X	US 4 818 421 A (BORIS FELICIA J ET AL) 4 April 1989 (1989-04-04) example 2 ----	1-7,9
X	EP 0 937 770 A (PROCTER & GAMBLE) 25 August 1999 (1999-08-25) examples 1-4 ----	1,2,4-9
X	US 4 873 002 A (IBRAHIM NADER) 10 October 1989 (1989-10-10) examples 1,2,5-7 ----- -/--	1,2,4-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 June 2003

Date of mailing of the international search report

20/06/2003

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Pentek, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/02700

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 004 121 A (PROCTER & GAMBLE) 19 September 1979 (1979-09-19) examples I, IV, V, VII ----	1, 2, 4-7
X	EP 0 021 491 A (PROCTER & GAMBLE) 7 January 1981 (1981-01-07) examples IV-VI ----	1, 2, 4-7
X	WO 99 35223 A (WITCO CORPORATION (US); WITCO SURFACTANTS GMBH (DE)) 15 July 1999 (1999-07-15) example 9 ----	1, 2, 4-6, 8
X	WO 88 04341 A (FINK JEAN MARIE; LACKE PHILIP M (US)) 16 June 1988 (1988-06-16) page 4, line 25 -page 5, line 34; examples ----	1-10
X	US 5 480 567 A (LAM ANDREW C ET AL) 2 January 1996 (1996-01-02) column 1, line 40-66; claim 1; examples -----	1-10

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/02700

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5066413	A	19-11-1991	US 5062973 A	05-11-1991
			US 4938879 A	03-07-1990
			US 5173200 A	22-12-1992
			CA 1315048 A1	30-03-1993
			WO 9011838 A1	18-10-1990
US 4818421	A	04-04-1989	AT 229188 A	15-05-1994
			AU 2229588 A	13-04-1989
			BE 1002291 A5	20-11-1990
			CH 678535 A5	30-09-1991
			DE 3832017 A1	27-04-1989
			DK 514588 A	18-03-1989
			FR 2637609 A1	13-04-1990
			GB 2210070 A ,B	01-06-1989
			GB 2245908 A ,B	15-01-1992
			GR 88100611 A ,B	22-06-1989
			IT 1224523 B	04-10-1990
			NL 8802301 A	17-04-1989
			SE 8803236 A	22-03-1989
EP 0937770	A	25-08-1999	EP 0937770 A1	25-08-1999
			WO 9942546 A1	26-08-1999
US 4873002	A	10-10-1989	AU 553455 B2	17-07-1986
			AU 1261983 A	31-05-1984
			BE 896261 A1	26-09-1983
			GR 78800 A1	02-10-1984
			PT 76369 A	01-04-1983
EP 0004121	A	19-09-1979	AT 183079 A	15-12-1986
			BE 59 T1	18-04-1980
			BR 7901558 A	16-10-1979
			CA 1109757 A1	29-09-1981
			CH 644891 A5	31-08-1984
			DE 2948921 A1	06-11-1980
			EP 0004121 A1	19-09-1979
			FR 2446314 A1	08-08-1980
			GB 2041968 A ,B	17-09-1980
			GR 73580 A1	21-03-1984
			IT 1148286 B	26-11-1986
			JP 54163907 A	27-12-1979
			MX 150469 A	14-05-1984
			NL 7915015 A	30-05-1980
			NL 7915015 T	30-05-1980
			SE 439494 B	17-06-1985
			SE 8001135 A	13-02-1980
EP 0021491	A	07-01-1981	CA 1131092 A1	07-09-1982
			EP 0021491 A1	07-01-1981
			JP 56038396 A	13-04-1981
WO 9935223	A	15-07-1999	AU 2105999 A	26-07-1999
			AU 2214999 A	26-07-1999
			BR 9906839 A	30-10-2001
			CA 2318561 A1	15-07-1999
			EP 1045891 A1	25-10-2000
			HU 0100282 A2	28-06-2001
			JP 2002500235 T	08-01-2002

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/02700

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9935223	A	NO 20003497 A	08-09-2000
		PL 342081 A1	21-05-2001
		SK 10542000 A3	06-11-2001
		WO 9935120 A1	15-07-1999
		WO 9935223 A1	15-07-1999
		US 6376455 B1	23-04-2002
WO 8804341	A	16-06-1988	WO 8804341 A1
			EP 0292483 A1
			US 4906410 A
US 5480567	A	02-01-1996	NONE