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(54) **Title**: FABRIC TREATMENT METHOD AND COMPOSITION

(57) **Abstract**: A fabric softening composition comprising a fabric softening compound and a switchable material capable of changing its hydrophobic-hydrophilic properties in response to an activation step, wherein the switchable material is present in an amount of from 0.1 to 50 wt %, based on the total weight of the composition and has a mean particle size of from 1 to 50 nm, provides comfort without loss of colour of dyed fabric.

# FABRIC TREATMENT METHOD AND COMPOSITION

## Technical Field

This invention relates to a method of treating a dyed fabric with a rinse conditioner composition comprising a switchable material and thereafter subjecting the fabric to an activation step, to cause differential hydrophobicity, thus encouraging transport of water through the fabric, without causing a detrimental effect to the colour of the dyed fabric. In one aspect the invention relates to compositions for use in such a method.

## Background and Prior Art

The uncomfortable feel of clothes associated with perspiration can take one of two forms depending on the level of sweat production. Under conditions of high sweat production, clothes can become saturated with sweat. Damp areas of clothing then contact the skin causing discomfort through local cooling and cling.

Under conditions of low sweat production there is sweat (high humidity) in any space between the skin and first layer of clothing and within the clothing immediately adjacent the skin. Water vapour will gradually diffuse through the clothing into the surrounding air.

The textile literature identifies a high humidity level in the space between the skin and the first layer of clothing as one of the key drivers of discomfort under ambient, low exercise conditions. Similarly, discomfort can arise from the build up of liquid water on the inside surface of apparel textiles.

A known approach to this problem is to increase the rate of liquid water transport through textile by increasing the rate of wicking or wetting. This is achieved by decreasing the contact angle of water on the fibre surface. This approach has the disadvantage of also increasing the total amount of water held in the textile. This leads to increased thermal conductivity and increased cling when these areas touch the skin. Both of these effects increase the discomfort experienced in wear.

It is known that certain materials, such as Zinc Oxide (ZnO) and Titanium Oxide ($TiO_2$) have the ability to change between hydrophobic and hydrophilic properties under different environmental conditions, see for example *J. Am. Chem. Soc 2004, 126, 62-63* and *Soft Matter 2005, 1, 55-61*. There are various publications describing the effect of ZnO and $TiO_2$ as hydrophobic-hydrophilic switchable surfaces. WO2004108846 describes the use of $TiO_2$ as a coating in combination with a siloxane for an easy clean surface and discloses that it can be applied to fabrics. US2005/0186871 A1 discloses a gas permeable apparatus comprising a structure including a plurality of surfaces, at least another of the surfaces comprising electrets, at least one light source for exposing the at least one of the surfaces comprising the photocatalyst to light photons sufficient to activate the photocatalyst, the structure allowing for filtering particulates, wicking liquids, disinfecting, and deodarizing the surfaces.

Our related patent EP2082089B1, also published as WO2008/058831, provides a composition for treating fabric with a rinse conditioner comprising an ester linked quaternary ammonium softening active and a hydrophilic-hydrophobic material comprising zinc oxide and/or titanium oxide, to increase transport of water through the fabric.

However, we have found that a further problem exists when this system is used on dyed textiles, namely that of a detrimental effect on the colour of the dyed textiles.

We have now surprisingly found that the use of switchable materials, having a specific particle size, in laundry products can lead to improved water transport properties of treated dyed textiles without detrimentally impacting the colour of the textiles.

Summary of the Invention

According to a first aspect of the invention there is provided a fabric softening composition comprising a fabric softening compound and a switchable material capable of changing its hydrophobic-hydrophilic properties in response to an activation step, wherein the switchable material is present in an amount of from 0.1 to 50 wt %, based on the total weight of the composition and has a particle size of from 1 to 50 nm.

According to a second aspect of the invention there is provided a method of treating a dyed fabric having a colour, comprising rinsing the dyed fabric in a composition as described in the first aspect of the invention to deposit fabric conditioner and switchable material thereon, drying the fabric and before, after or simultaneously with the drying, subjecting a portion of the fabric to an activation step to cause the switchable material deposited in said portion to undergo a change in its hydrophobic-hydrophilic properties, wherein said method does not have a detrimental effect on the colour of the dyed fabric.

The method preferably incorporates a switchable material selected from ZnO and $TiO_2$ with an activation step that comprises exposure to UV light. One side or portion of the fabric may be subjected to said activation step.

The composition works to increase comfort to the wearer by reducing the level of water held in the region of the textile next to the skin, at the same time as facilitating the movement of water through the textile. By depositing the switchable material onto the textile from the laundry treatment, areas which are close to the skin can be made hydrophobic, whereas areas of textile away from the skin may be rendered hydrophilic by an activation step. It is preferred the activation step uses local environmental conditions. For example, in a preferred embodiment the switchable material is photosensitive and the outside of the garment is exposed to light, particularly UV light, and is rendered hydrophilic, whilst the inside of the garment close to the skin and therefore shielded from the sunlight remains hydrophobic.

However, the deposition of these switchable materials onto dyed textiles can lead to a reduction in perceived depth of colour of the textile.

The Switchable Material

In principle any material which can be deposited on a fabric from a rinse conditioner which can "switch" properties from hydrophobic to hydrophilic or visa versa upon exposure to certain conditions may be employed in the invention. The activation step causing the switch in properties may be based upon photosensitivity, pH change, temperature change, heat flow, change in ionic strength, enzymatic activity etc. The most convenient activation step is based upon photosensitivity, particularly UV light, since it is readily possible to expose

the outside of a garment to sunlight, during wear and or drying, whilst shielding the inside of the garment.

Preferred switchable materials are ZnO and $TiO_2$ which can be drawn from a range of morphologies, shapes and aspect ratios. Other suitable switchable materials include those which undergo:

1) structural rearrangement to increase hydrophilicity (e.g. Ketoenol tautomerism or *cis-trans* isomerism resulting in breaking intra-molecular hydrogen bonds and favouring inter-molecular hydrogen bonds); or

2) degradation to more polar species (e.g. UV unstable dyes, or sunscreens).

The switchable materials are generally deposited to apply from 0.2 to 1 %, preferably 0.2 to 0.5 % by weight of the fabric after drying. The switchable materials are generally present in an amount of from 0.1 to 50 wt %, preferably 0.1 to 10 wt%, more preferably 0.1 to 5 wt % and most preferably from 0.1 to 4.5 wt % by total weight of the fabric softening composition.

The switchable material has a mean particle size of from 1 to 50 nm, preferably from 1 to 25 nm and most preferably from 1 to 10nm. The particle size may be measured using any suitable technique, which will be apparent to the skilled person, for example, BET gas absorption or dynamic light scattering techniques.

A preferred material is $TiO_2$ PCX-S7 (ex. Cristal Global), which has a particle size 6-10 nm.

Fabric Softening Compound

The conditioning agents (also referred to herein as a fabric softening active) may be cationic or non-ionic.

Fabric conditioning compositions in accordance with the invention may be dilute or concentrated. Dilute products typically contain up to about 8 %, generally about 2 to 8 % by weight of softening active, whereas concentrated products may contain up to about 50 wt %, preferably from about 8 to about 50 %, more preferably from 8 to 25 % by weight active. Compositions of more than about 25 % by weight of active are defined as "super concentrated", depending on the active system, and are also intended to be covered by the present invention. The fabric conditioning agent may, for example, be used in amounts of from 0.5 % to 35 %, preferably from 2 % to 30 % more preferably from 5 % to 25 % and most preferably from 8 % to 20 % by weight of the composition.

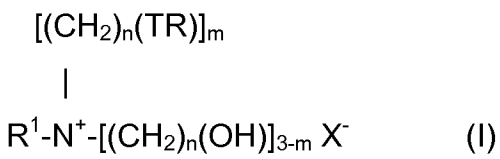
The preferred softening active for use in rinse conditioner compositions of the invention is a quaternary ammonium compound (QAC). The preferred quaternary ammonium fabric conditioner for use in compositions of the present invention are the so called “ester quats”.

Particularly preferred materials are the ester-linked triethanolamine (TEA) quaternary ammonium compounds comprising a mixture of mono-, di- and tri-ester linked components.

Typically, TEA-based fabric softening compounds comprise a mixture of mono, di- and tri-ester forms of the compound where the di-ester linked component comprises no more than 70 % by weight of the fabric softening compound, preferably no more than 60 wt % of the fabric softening compound and at least 10

% of the monoester linked component. A preferred hardened type of active has a typical mono:di:tri ester distribution in the range of from 12 to 25 mono: from 55 to 65 di: from 15 to 27 tri. A soft TEA quat may have a typical mono:di:tri ester distribution of from 25 to 45 %, preferably from 30 to 40 % mono: from 45 to 60 %, preferably from 50 to 55 % di: and from 5 to 25 %, preferably from 10 to 15 % tri; for example 40:60:10.

A first group of quaternary ammonium compounds (QACs) suitable for use in the present invention is represented by formula (I):



(I)

wherein each R is independently selected from a $C_{5-35}$ alkyl or alkenyl group; $R^1$ represents a $C_{1-4}$ alkyl, $C_{2-4}$ alkenyl or a $C_{1-4}$ hydroxyalkyl group; T is generally O-CO. (i.e. an ester group bound to R *via* its carbon atom), but may alternatively be CO-O (i.e. an ester group bound to R *via* its oxygen atom); n is a number selected from 1 to 4; m is a number selected from 1, 2, or 3; and $X^-$ is an anionic counter-ion, such as a halide or alkyl sulphate, e.g. chloride or methylsulphate. Di-esters variants of formula I (i.e. m = 2) are preferred and typically have mono- and tri-ester analogues associated with them. Such materials are particularly suitable for use in the present invention.

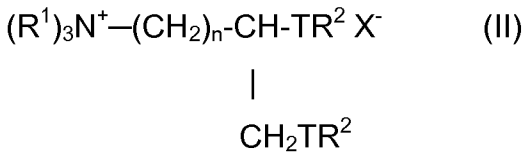
Especially preferred agents are preparations which are rich in the di-esters of triethanolammonium methylsulphate, otherwise referred to as “TEA ester quats”.

Commercial examples include Stepantex™ UL85, ex Stepan, Prapagen™ TQL, *ex* Clariant, and Tetranyl™ AHT-1, *ex* Kao, (both di-[hardened tallow ester] of

triethanolammonium methylsulphate), AT-1 (di-[tallow ester] of triethanolammonium methylsulphate), and L5/90 (di-[palm ester] of triethanolammonium methylsulphate), both *ex* Kao, and Rewoquat™ WE15 (a di-ester of triethanolammonium methylsulphate having fatty acyl residues deriving from $C_{10}$-$C_{20}$ and $C_{16}$-$C_{18}$ unsaturated fatty acids), *ex* Witco Corporation.

Also, soft quaternary ammonium actives such as Stepantex VK90, Stepantex VT90, SP88 (ex-Stepan), Prapagen TQ (ex-Clariant), Dehyquart AU-57 (ex-Cognis), Rewoquat WE18 (ex-Degussa) and Tetranyl L190 P, Tetranyl L190 SP and Tetranyl L190 S (all ex-Kao) are suitable.

A second group of QACs suitable for use in the invention is represented by formula (II):



(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; and wherein n, T, and $X^-$ are as defined above.

Preferred materials of this second group include 1,2 *bis*[tallowoyloxy]-3-trimethylammonium propane chloride, 1,2 *bis*[hardened tallowoyloxy]-3-trimethylammonium propane chloride, 1,2-*bis*[oleoyloxy]-3-trimethylammonium propane chloride, and 1,2 *bis*[stearoyloxy]-3-trimethylammonium propane chloride. Such materials are described in US 4,137,180 (Lever Brothers). Preferably, these materials also comprise an amount of the corresponding mono-ester.

A third group of QACs suitable for use in the invention is represented by formula (III):

$(R^1)_2$-$N^+$-$[(CH_2)_n$-T-$R^2]_2$ $X^-$ (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; and n, T, and $X^-$ are as defined above. Preferred materials of this third group include bis(2-tallowoyloxyethyl)dimethyl ammonium chloride, partially hardened and hardened versions thereof.

The iodine value of the quaternary ammonium fabric conditioning material is preferably from 0 to 80, more preferably from 0 to 60, and most preferably from 0 to 45. The iodine value may be chosen as appropriate. Essentially saturated material having an iodine value of from 0 to 5, preferably from 0 to 1 may be used in the compositions of the invention. Such materials are known as "hardened" quaternary ammonium compounds.

A further preferred range of iodine values is from 20 to 60, preferably 25 to 50, more preferably from 30 to 45. A material of this type is a "soft" triethanolamine quaternary ammonium compound, preferably triethanolamine di-alkylester methylsulphate. Such ester-linked triethanolamine quaternary ammonium compound comprise unsaturated fatty chains.

Iodine value as used in the context of the present invention refers to the measurement of the degree of unsaturation present in a material by a method of nmr spectroscopy as described in Anal. Chem., 34, 1136 (1962) Johnson and Shoolery.

Iodine value is defined as the number of grams of iodine absorbed per 100g of the test material. Olefinic materials absorb 1 gram of iodine per atom of olefinic hydrogen. Hence measurement can be converted to the equivalent Iodine Value. The hydrogen nmr spectrum at 360 MHz is obtained for the test material. The integral intensity, $I_s$, of the band derived from olefinic hydrogen in the alkyl chain and the integral intensity, $I_m$, of the band derived from terminal methyl groups in the alkyl chains are measured.

The number of olefinic hydrogens per molecule is given by:

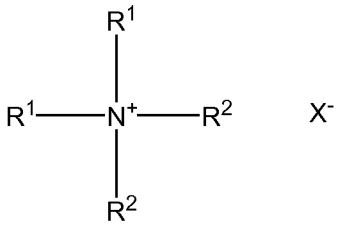
$$\frac{I_s}{I_m} \times 6$$

and the Iodine Value is given by:

$$\frac{I_s \times 127 \times 100 \times 6}{I_m \times MMW}$$

where MMW is the mean molecular weight of the test material.

A further type of softening compound is a non-ester quaternary ammonium material represented by formula (IV):-

(IV) 

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

**Oily sugar derivatives**

The compositions of the invention may contain a non-cationic softening material, which is preferably an oily sugar derivative. An oily sugar derivative is a liquid or soft solid derivative of a cyclic polyol (CPE) or of a reduced saccharide (RSE), said derivative resulting from 35 to 100 % of the hydroxyl groups in said polyol or in said saccharide being esterified or etherified. The derivative has two or more ester or ether groups independently attached to a $C_8$-$C_{22}$ alkyl or alkenyl chain.

Advantageously, the CPE or RSE does not have any substantial crystalline character at 20°C. Instead it is preferably in a liquid or soft solid state as herein defined at 20°C.

The liquid or soft solid (as hereinafter defined) CPEs or RSEs suitable for use in the present invention result from 35 to 100% of the hydroxyl groups of the starting cyclic polyol or reduced saccharide being esterified or etherified with groups such

that the CPEs or RSEs are in the required liquid or soft solid state. These groups typically contain unsaturation, branching or mixed chain lengths.

Typically the CPEs or RSEs have 3 or more ester or ether groups or mixtures thereof, for example 3 to 8, especially 3 to 5. It is preferred if two or more of the ester or ether groups of the CPE or RSE are independently of one another attached to a $C_8$ to $C_{22}$ alkyl or alkenyl chain. The $C_8$ to $C_{22}$ alkyl or alkenyl groups may be branched or linear carbon chains.

Preferably 35 to 85 % of the hydroxyl groups, most preferably 40-80 %, even more preferably 45-75 %, such as 45-70 % are esterified or etherified.

Preferably the CPE or RSE contains at least 35 % tri or higher esters, eg at least 40 %.

The CPE or RSE has at least one of the chains independently attached to the ester or ether groups having at least one unsaturated bond. This provides a cost effective way of making the CPE or RSE a liquid or a soft solid. It is preferred if predominantly unsaturated fatty chains, derived from, for example, rape oil, cotton seed oil, soybean oil, oleic, tallow, palmitoleic, linoleic, erucic or other sources of unsaturated vegetable fatty acids, are attached to the ester/ether groups.

These chains are referred to below as the ester or ether chains (of the CPE or RSE).

The ester or ether chains of the CPE or RSE are preferably predominantly unsaturated. Preferred CPEs or RSEs include sucrose tetratallowate, sucrose tetrarapeate, sucrose tetraoleate, sucrose tetraesters of soybean oil or cotton seed oil, cellobiose tetraoleate, sucrose trioleate, sucrose triapeate, sucrose

pentaoleate, sucrose pentarapeate, sucrose hexaoleate, sucrose hexarapeate, sucrose triesters, pentaesters and hexaesters of soybean oil or cotton seed oil, glucose tiroleate, glucose tetraoleate, xylose trioleate, or sucrose tetra-,tri-, penta- or hexa- esters with any mixture of predominantly unsaturated fatty acid chains. The most preferred CPEs or RSEs are those with monounsaturated fatty acid chains, i.e. where any polyunsaturation has been removed by partial hydrogenation. However some CPEs or RSEs based on polyunsaturated fatty acid chains, e.g. sucrose tetralinoleate, may be used provided most of the polyunsaturation has been removed by partial hydrogenation.

The most highly preferred liquid CPEs or RSEs are any of the above but where the polyunsaturation has been removed through partial hydrogenation.

Preferably 40 % or more of the fatty acid chains contain an unsaturated bond, more preferably 50 % or more, most preferably 60% or more. In most cases 65 % to 100 %, e.g. 65 % to 95 % contain an unsaturated bond.

CPEs are preferred for use with the present invention. Inositol is a preferred example of a cyclic polyol. Inositol derivatives are especially preferred.

In the context of the present invention, the term cyclic polyol encompasses all forms of saccharides. Indeed saccharides are especially preferred for use with this invention. Examples of preferred saccharides for the CPEs or RSEs to be derived from are monosaccharides and disaccharides.

Examples of monosaccharides include xylose, arabinose, galactose, fructose, sorbose and glucose. Glucose is especially preferred. Examples of disaccharides include maltose, lactose, cellobiose and sucrose. Sucrose is especially preferred. An example of a reduced saccharide is sorbitan.

The liquid or soft solid CPEs can be prepared by methods well known to those skilled in the art. These include acylation of the cyclic polyol or reduced saccharide with an acid chloride; trans-esterification of the cyclic polyol or reduced saccharide fatty acid esters using a variety of catalysts; acylation of the cyclic polyol or reduced saccharide with an acid anhydride and acylation of the cyclic polyol or reduced saccharide with a fatty acid. See for instance US 4 386 213 and AU 14416/88 (both P&G).

It is preferred if the CPE or RSE has 3 or more, preferably 4 or more ester or ether groups. If the CPE is a disaccharide it is preferred if the disaccharide has 3 or more ester or ether groups. Particularly preferred CPEs are esters with a degree of esterification of 3 to 5, for example, sucrose tri, tetra and penta esters.

Where the cyclic polyol is a reducing sugar it is advantageous if each ring of the CPE has one ether or ester group, preferably at the $C_1$ position. Suitable examples of such compounds include methyl glucose derivatives.

Examples of suitable CPEs include esters of alkyl(poly)glucosides, in particular alkyl glucoside esters having a degree of polymerisation of 2.

The length of the unsaturated (and saturated if present) chains in the CPE or RSE is $C_8$-$C_{22}$, preferably $C_{12}$-$C_{22}$. It is possible to include one or more chains of $C_1$-$C_8$, however these are less preferred.

The liquid or soft solid CPEs or RSEs which are suitable for use in the present invention are characterised as materials having a solid:liquid ratio of between 50:50 and 0:100 at 20°C as determined by $T_2$ relaxation time NMR, preferably between 43:57 and 0:100, most preferably between 40:60 and 0:100, such as, 20:80 and 0:100. The $T_2$ NMR relaxation time is commonly used for

characterising solid:liquid ratios in soft solid products such as fats and margarines. For the purpose of the present invention, any component of the signal with a $T_2$ of less than 100 μs is considered to be a solid component and any component with $T_2 \geq 100$ μs is considered to be a liquid component.

For the CPEs and RSEs, the prefixes (e.g. tetra and penta) only indicate the average degrees of esterification. The compounds exist as a mixture of materials ranging from the monoester to the fully esterified ester. It is the average degree of esterification which is used herein to define the CPEs and RSEs.

The HLB of the CPE or RSE is typically between 1 and 3.

Where present, the CPE or RSE is preferably present in the composition in an amount of 0.5-50% by weight, based upon the total weight of the composition, more preferably 1-30% by weight, such as 2-25%, e.g. 2-20%.

The CPEs and RSEs for use in the compositions of the invention include sucrose tetraoleate, sucrose pentaerucate, sucrose tetraerucate and sucrose pentaoleate.

**Co-softeners and fatty complexing agents**

Co-softeners may be used. When employed, they are typically present at from 0.1 to 20% and particularly at from 0.5 to 10%, based on the total weight of the composition. Preferred co-softeners include fatty esters, and fatty N-oxides. Fatty esters that may be employed include fatty monoesters, such as glycerol monostearate, fatty sugar esters, such as those disclosed WO 01/46361 (Unilever).

The compositions for use in the present invention may comprise a fatty complexing agent.

Especially suitable fatty complexing agents include fatty alcohols and fatty acids. Of these, fatty alcohols are most preferred.

Fatty complexing material may be used to improve the viscosity profile of the composition.

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).

The fatty complexing agent is preferably present in an amount greater than 0.3 to 5% by weight based on the total weight of the composition. More preferably, the fatty component is present in an amount of from 0.4 to 4%. The weight ratio of the mono-ester component of the quaternary ammonium fabric softening material to the fatty complexing agent is preferably from 5:1 to 1:5, more preferably 4:1 to 1:4, most preferably 3:1 to 1:3, e.g. 2:1 to 1:2.

**Non-ionic surfactant**

The compositions may further comprise a nonionic surfactant. Typically these can be included for the purpose of stabilising the compositions. These are particularly suitable for compositions comprising hardened quaternary ammonium compounds.

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

$$R\text{-}Y\text{-}(C_2H_4O)_z\text{-}CH_2\text{-}CH_2\text{-}OH$$

where R is selected from the group consisting of primary, secondary and branched chain alkyl and/or acyl hydrocarbyl groups (when Y = -C(O)O, R ≠ an acyl hydrocarbyl group); 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.

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

-O- , -C(O)O- , -C(O)N(R)- or -C(O)N(R)R-

in which R has the meaning given above or can be hydrogen; and Z is at least about 8, preferably at least about 10 or 11.

Preferably the nonionic surfactant has an HLB of from about 7 to about 20, more preferably from 10 to 18, e.g. 12 to 16. Genapol™ C200 (Clariant) based on coco chain and 20 EO groups is an example of a suitable nonionic surfactant.

If present, the nonionic surfactant is present in an amount from 0.01 to 10%, more preferably 0.1 to 5 by weight, based on the total weight of the composition.

**Shading Dyes**

Optional shading dyes can be used. Preferred dyes are violet or blue. Suitable and preferred classes of dyes are discussed below. Moreover the unsaturated quaternary ammonium compounds are subject to some degree of UV light and/or transition metal ion catalysed radical auto-oxidation, with an attendant risk of yellowing of fabric. The presence of a shading dye also reduces the risk of yellowing from this source.

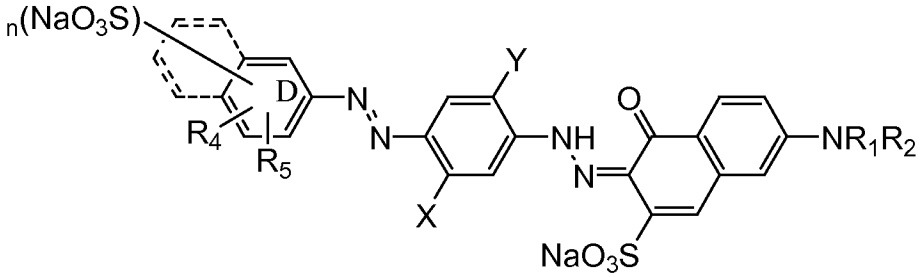
Different shading dyes give different levels of colouring. The level of shading dye present in the compositions of the present invention depend, therefore, on the type of shading dye. Preferred overall ranges, suitable for the present invention are from 0.00001 to 0.1 wt %, more preferably 0.0001 to 0.01 wt %, most preferably 0.0005 to 0.005 wt % by weight of the total composition.

**Direct Dyes**

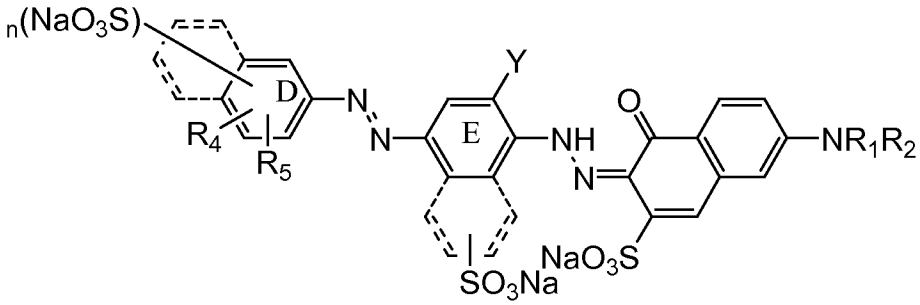
Direct dyes (otherwise known as substantive dyes) are the class of water soluble dyes which have an affinity for fibres and are taken up directly. Direct violet and direct blue dyes are preferred.

Preferably the dye are *bis*-azo or *tris*-azo dyes are used.

Most preferably, the direct dye is a direct violet of the following structures:



or



wherein:

ring D and E may be independently naphthyl or phenyl as shown;

$R_1$ is selected from: hydrogen and C1-C4-alkyl, preferably hydrogen;

$R_2$ is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;

$R_3$ and $R_4$ are independently selected from: hydrogen and C1-C4-alkyl, preferably hydrogen or methyl;

X and Y are independently selected from: hydrogen, C1-C4-alkyl and C1-C4-alkoxy; preferably the dye has X= methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

Preferred dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51,

and direct violet 99. Bis-azo copper containing dyes such as direct violet 66 may be used.

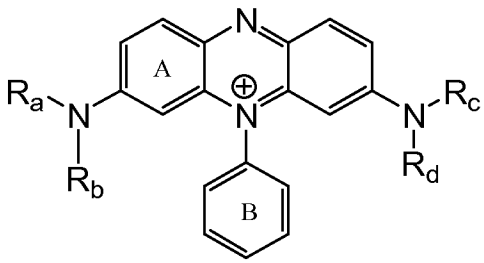
The benzidene based dyes are less preferred.

Preferably the direct dye is present at 0.00001 wt% to 0.0010 wt% of the formulation.

In another embodiment the direct dye may be covalently linked to the photo-bleach, for example as described in WO2006/024612.

**Acid dyes**

Cotton substantive acid dyes give benefits to cotton containing garments. Preferred dyes and mixes of dyes are blue or violet. Preferred acid dyes are:
(i) azine dyes, wherein the dye is of the following core structure:




wherein $R_a$, $R_b$, $R_c$ and $R_d$ are selected from: H, a branched or linear C1 to C7-alkyl chain, benzyl a phenyl, and a naphthyl;
the dye is substituted with at least one $SO_3^-$ or $-COO^-$ group;
the B ring does not carry a negatively charged group or salt thereof;
and the A ring may further substituted to form a naphthyl;

the dye is optionally substituted by groups selected from: amine, methyl, ethyl, hydroxyl, methoxy, ethoxy, phenoxy, Cl, Br, I, F, and $NO_2$.

Preferred azine dyes are: acid blue 98, acid violet 50, and acid blue 59, more preferably acid violet 50 and acid blue 98.

Other preferred non-azine acid dyes are acid violet 17, acid black 1 and acid blue 29.

Preferably the acid dye is present at 0.0005 wt% to 0.01 wt% of the formulation.

**Hydrophobic dyes**

The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, napthoquinone, anthraquinone and mono-azo or di-azo dye chromophores. Hydrophobic dyes are dyes which do not contain any charged water solubilising group. Hydrophobic dyes may be selected from the groups of disperse and solvent dyes. Blue and violet anthraquinone and mono-azo dye are preferred.

Preferred dyes include solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.

Preferably the hydrophobic dye is present at 0.0001 wt% to 0.005 wt% of the formulation.

**Basic dyes**

Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. They are of particular utility for used in composition that contain predominantly cationic surfactants. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International.

Preferred examples include triarylmethane basic dyes, methane basic dye, anthraquinone basic dyes, basic blue 16, basic blue 65, basic blue 66, basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48; basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141.

**Reactive dyes**

Reactive dyes are dyes which contain an organic group capable of reacting with cellulose and linking the dye to cellulose with a covalent bond. They deposit onto cotton.

Preferably the reactive group is hydrolysed or reactive group of the dyes has been reacted with an organic species such as a polymer, so as to the link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.

Preferred examples include reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue 96.

**Dye conjugates**

Dye conjugates are formed by binding direct, acid or basic dyes to polymers or particles via physical forces.

Dependent on the choice of polymer or particle they deposit on cotton or synthetics. A description is given in WO2006/055787. They are not preferred.

Particularly preferred dyes are: direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, direct violet 99, acid blue 98, acid violet 50, acid blue 59, acid violet 17, acid black 1, acid blue 29, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63, disperse violet 77 and mixtures thereof.

**Perfume**

The compositions of the present invention may comprise one or more perfumes if desired. The perfume is preferably present in an amount from 0.01 to 10 % by weight, more preferably from 0.05 to 5 % by weight, even more preferably from 0.1 to 4.0 %, most preferably from 0.15 to 4.0 % by weight, based on the total weight of the composition.

Useful components of the perfume include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components may be found in the current literature, e.g., in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA). These substances are well known to the person skilled in the art of perfuming, flavouring, and/or aromatizing consumer

products, i.e., of imparting an odour and/or a flavour or taste to a consumer product traditionally perfumed or flavoured, or of modifying the odour and/or taste of said consumer product.

By perfume in this context is not only meant a fully formulated product fragrance, but also selected components of that fragrance, particularly those which are prone to loss, such as the so-called 'top notes'.

Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Examples of well known top-notes include citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol. Top notes typically comprise 15-25%wt of a perfume composition and in those embodiments of the invention which contain an increased level of top-notes it is envisaged at that least 20%wt would be present within the encapsulate.

Some or all of the perfume or pro-fragrance may be encapsulated, typical perfume components which it is advantageous to encapsulate, include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100-250 Celsius and pro-fragrances which can produce such components.

It is also advantageous to encapsulate perfume components which have a low Clog P (i.e. those which will be partitioned into water), preferably with a Clog P of less than 3.0. These materials, of relatively low boiling point and relatively low Clog P have been called the "delayed blooming" perfume ingredients and include the following materials:

Allyl Caproate, Amyl Acetate, Amyl Propionate, Anisic Aldehyde, Anisole, Benzaldehyde, Benzyl Acetate, Benzyl Acetone, Benzyl Alcohol, Benzyl Formate,

Benzyl Iso Valerate, Benzyl Propionate, Beta Gamma Hexenol, Camphor Gum, Laevo-Carvone, d-Carvone, Cinnamic Alcohol, Cinamyl Formate, Cis-Jasmone, cis-3-Hexenyl Acetate, Cuminic Alcohol, Cyclal C, Dimethyl Benzyl Carbinol, Dimethyl Benzyl Carbinol Acetate, Ethyl Acetate, Ethyl Aceto Acetate, Ethyl Amyl Ketone, Ethyl Benzoate, Ethyl Butyrate, Ethyl Hexyl Ketone, Ethyl Phenyl Acetate, Eucalyptol, Eugenol, Fenchyl Acetate, Flor Acetate (tricyclo Decenyl Acetate), Frutene (tricyclco Decenyl Propionate), Geraniol, Hexenol, Hexenyl Acetate, Hexyl Acetate, Hexyl Formate, Hydratropic Alcohol, Hydroxycitronellal, Indone, Isoamyl Alcohol, Iso Menthone, Isopulegyl Acetate, Isoquinolone, Ligustral, Linalool, Linalool Oxide, Linalyl Formate, Menthone, Menthyl Acetphenone, Methyl Amyl Ketone, Methyl Anthranilate, Methyl Benzoate, Methyl Benyl Acetate, Methyl Eugenol, Methyl Heptenone, Methyl Heptine Carbonate, Methyl Heptyl Ketone, Methyl Hexyl Ketone, Methyl Phenyl Carbinyl Acetate, Methyl Salicylate, Methyl-N-Methyl Anthranilate, Nerol, Octalactone, Octyl Alcohol, p-Cresol, p-Cresol Methyl Ether, p-Methoxy Acetophenone, p-Methyl Acetophenone, Phenoxy Ethanol, Phenyl Acetaldehyde, Phenyl Ethyl Acetate, Phenyl Ethyl Alcohol, Phenyl Ethyl Dimethyl Carbinol, Prenyl Acetate, Propyl Bornate, Pulegone, Rose Oxide, Safrole, 4-Terpinenol, Alpha-Terpinenol, and/or Viridine.

Preferred non-encapsulated perfume ingredients are those hydrophobic perfume components with a ClogP above 3. As used herein, the term "ClogP" means the calculated logarithm to base 10 of the octanol/water partition coefficient (P). The octanol/water partition coefficient of a perfume raw material (PRM) is the ratio between its equilibrium concentrations in octanol and water. Given that this measure is a ratio of the equilibrium concentration of a PRM in a non-polar solvent (octanol) with its concentration in a polar solvent (water), ClogP is also a measure of the hydrophobicity of a material--the higher the ClogP value, the more hydrophobic the material. ClogP values can be readily calculated from a program called "CLOGP" which is available from Daylight Chemical Information Systems

Inc., Irvine Calif., USA. Octanol/water partition coefficients are described in more detail in U.S. Pat. No. 5,578,563.

Perfume components with a ClogP above 3 comprise: Iso E super, citronellol, Ethyl cinnamate, Bangalol, 2,4,6-Trimethylbenzaldehyde, Hexyl cinnamic aldehyde, 2,6-Dimethyl-2-heptanol, Diisobutylcarbinol, Ethyl salicylate, Phenethyl isobutyrate, Ethyl hexyl ketone, Propyl amyl ketone, Dibutyl ketone, Heptyl methyl ketone, 4,5-Dihydrotoluene, Caprylic aldehyde, Citral, Geranial, Isopropyl benzoate, Cyclohexanepropionic acid, Campholene aldehyde, Caprylic acid, Caprylic alcohol, Cuminaldehyde, 1-Ethyl-4-nitrobenzene, Heptyl formate, 4-Isopropylphenol, 2-Isopropylphenol, 3-Isopropylphenol, Allyl disulfide, 4-Methyl-1-phenyl-2-pentanone, 2-Propylfuran, Allyl caproate, Styrene, Isoeugenyl methyl ether, Indonaphthene, Diethyl suberate, L-Menthone, Menthone racemic, p-Cresyl isobutyrate, Butyl butyrate, Ethyl hexanoate, Propyl valerate, n-Pentyl propanoate, Hexyl acetate, Methyl heptanoate, trans-3,3,5-Trimethylcyclohexanol, 3,3,5-Trimethylcyclohexanol, Ethyl p-anisate, 2-Ethyl-1-hexanol, Benzyl isobutyrate, 2,5-Dimethylthiophene, Isobutyl 2-butenoate, Caprylnitrile, gamma-Nonalactone, Nerol, trans-Geraniol, 1-Vinylheptanol, Eucalyptol, 4-Terpinenol, Dihydrocarveol, Ethyl 2-methoxybenzoate, Ethyl cyclohexanecarboxylate, 2-Ethylhexanal, Ethyl amyl carbinol, 2-Octanol, 2-Octanol, Ethyl methylphenylglycidate, Diisobutyl ketone, Coumarone, Propyl isovalerate, Isobutyl butanoate, Isopentyl propanoate, 2-Ethylbutyl acetate, 6-Methyl-tetrahydroquinoline, Eugenyl methyl ether, Ethyl dihydrocinnamate, 3,5-Dimethoxytoluene, Toluene, Ethyl benzoate, n-Butyrophenone, alpha-Terpineol, Methyl 2-methylbenzoate, Methyl 4-methylbenzoate, Methyl 3, methylbenzoate, sec. Butyl n-butyrate, 1,4-Cineole, Fenchyl alcohol, Pinanol, cis-2-Pinanol, 2,4, Dimethylacetophenone, Isoeugenol, Safrole, Methyl 2-octynoate, o-Methylanisole, p-Cresyl methyl ether, Ethyl anthranilate, Linalool, Phenyl butyrate, Ethylene glycol dibutyrate, Diethyl phthalate, Phenyl mercaptan, Cumic alcohol, m-Toluquinoline, 6-Methylquinoline,

Lepidine, 2-Ethylbenzaldehyde, 4-Ethylbenzaldehyde, o-Ethylphenol, p-Ethylphenol, m-Ethylphenol, (+)-Pulegone, 2,4-Dimethylbenzaldehyde, Isoxylaldehyde, Ethyl sorbate, Benzyl propionate, 1,3-Dimethylbutyl acetate, Isobutyl isobutanoate, 2,6-Xylenol, 2,4-Xylenol, 2,5-Xylenol, 3,5-Xylenol, Methyl cinnamate, Hexyl methyl ether, Benzyl ethyl ether, Methyl salicylate, Butyl propyl ketone, Ethyl amyl ketone, Hexyl methyl ketone, 2,3-Xylenol, 3,4, Xylenol, Cyclopentadenanolide and Phenyl ethyl 2 phenylacetate 2.

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components from the list given of delayed blooming perfumes given above and/or the list of perfume components with a ClogP above 3 present in the perfume.

Another group of perfumes with which the present invention can be applied are the so-called 'aromatherapy' materials. These include many components also used in perfumery, including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian.

**Further Optional Ingredients**

The compositions of the invention may contain one or more other ingredients. Such ingredients include further preservatives (e.g. bactericides), pH buffering agents, perfume carriers, hydrotropes, anti-redeposition agents, soil-release agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, silicones, antifoams, colourants, pearlisers and/or opacifiers, natural

oils/extracts, processing aids, e.g. electrolytes, hygiene agents, e.g. anti-bacterials and antifungals, thickeners and skin benefit agents.

Product Use

The compositions of the present invention are preferably rinse conditioner compositions and may be used in the rinse cycle of a domestic laundry process.

The composition is preferably used in the rinse cycle of a home textile laundering operation, where, it may be added directly in an undiluted state to a washing machine, e.g. through a dispenser drawer or, for a top-loading washing machine, directly into the drum. Alternatively, it can be diluted prior to use. The compositions may also be used in a domestic hand-washing laundry operation.

It is also possible, though less desirable, for the compositions of the present invention to be used in industrial laundry.

The invention will be described with reference to the following Example.

Example

Apparatus

Pad Mangle : Vertical laboratory padder VFM type ex. Werner Mathis AG
Darkened Drying frame
Light Source : Atlas Xenon Weatherometer S3000
Bottle roller: Stuart Scientific Roller mixer SRT1
Spin dryer: Creda Debonair spindryer

Materials

**Fabric** : 100% Polyester (Knit 140gm$^{-2}$)

**Treatments** :2 types of titanium dioxide were used in the treatment of the fabric:- $TiO_2$ nanopowder (ex. Sigma Aldrich) of particle size of approximately 100 nm. $TiO_2$ PCX-S7 (ex. Cristal Global)of particle size 6-10 nm.

**Example 1:- Preparation of Fabric Conditioners 1 and 2 in accordance with the invention and Comparative Examples A and B.**

Compositions 1, 2, A and B were dilute liquid fabric conditioners. The compositions are shown in Table 1.

**Table 1: Composition of Fabric Conditioners 1 and 2 in accordance with the invention and Comparative Examples A and B.**

| Material | Composition (wt %) | | | |
|---|---|---|---|---|
| | **A** | **1** | **B** | **2** |
| $TiO_2$ nanopowder | 50.00 | - | 2.5 | - |
| $TiO_2$ PCX-S7 | - | 50.00 | - | 2.5 |
| Cationic Fabric Softener; TEP-88L[1] | 5.68 | 5.68 | 5.68 | 5.68 |
| Tallow alcohol (Stenol 1618) | 0.32 | 0.32 | 0.32 | 0.32 |
| Water + perfume | to 100 | to 100 | to 100 | to 100 |

([1] Palm based soft TEA Quat, ex FXG)

**Example 2:- Treatement of dyed fabrics with Fabric Conditioners 1 and 2 in accordance with the invention and Comparative Examples A and B.**

**Treatment**

Samples of clean red polyester were cut into 20cm x 20cm pieces.

Fabric samples were treated with prototypes using a pad mangle or a bottle roller.

**Padded Application**

The Fabric Softeners 1 and A were diluted to make a 25% w/w dispersions for further dilution.

This 25% dispersion was further diluted to make a 2% w/w dispersion for pad application.

The 2% w/w dispersion was pad applied to the polyester at 100% pick-up.

This evenly delivered 1.0% on weight of fabric (o.w.f.) of the metal oxide and 0.116 % o.w.f. of standard rinse conditioner active to the fabric.

**Exhaust Application**

Fabric Softeners 1 and A were diluted to make a 25% w/w dispersion for further dilution.

This 25% dispersion was diluted to make 0.25% w/w dispersion for exhaust application.

The 0.25% w/w dispersion placed in a bottle with a fabric sample.

The bottle was rolled for 10 minutes to allow deposition to take place.

The fabric sample was then spun for 15 seconds in a domestic spin dryer.

This delivered 1.0% o.w.f. of the metal oxide and 0.116% o.w.f. of standard rinse conditioner active to the fabric if 100% of the material is deposited.

The treated fabric samples were allowed to dry in air within a darkened drying frame.

**Light Exposure**

The treated dried samples were then cut in half; one half was left in the darkened drying frame whilst the other half was placed in the Atlas weatherometer mounting frame ready for light exposure.

The fabric samples were then exposed to a 2kW Xenon light source for 3 hours with a relative humidity of from 60 to 80%.

Once the exposure was complete the polyester samples were assessed for their wetting behaviour.

**Example 3:- Wetting behaviour of fabric treated with Composition 1 and Comparative Example A**

A wetting test was carried out to illustrate the known ability of $TiO_2$, of two different particle sizes, to confer hydrophilic-hydrophobic properties to fabric.

**Wetting Test**

Exposed and unexposed samples were assessed for wetting.

Several 50μl droplets were placed across the surface of the fabric and the time taken for the droplets to fully penetrate the surface was measured. This was completed on both sides of the fabric.

Results, shown as time taken to wet the surface against treatment, are given in Table 2 below.

**Table 2: Wetting time for fabric (knitted polyester) treated with compositions 1 and A.**

| **Treatments, padded onto fabric** | **Wetting Time (seconds)** |
|---|---|
| Comparative A | > 600 |
| Comparative A + UV exposure | 0 |
| Comparative A + UV exposure (reverse side of fabric) | > 600 |
| Composition 1 | > 600 |
| Composition 1 + UV exposure | 0 |
| Composition 1 + UV exposure (reverse side of fabric) | > 600 |
| Untreated (Control) | > 600 |
| Untreated + UV exposure (Control) | > 600 |

0 indicates instantaneous wetting (i.e. a hydrophilic surface); > 600 equates to a highly hydrophobic fabric surface.

Table 2 shows that the $TiO_2$ particles on the fabric confer a hydrophilic-hydrophobic switching effect, regardless of particle size.

**Example 4:- Colour of fabric treated with Composition 1 and Comparative Example A**

**Colour measurement**

Measurement of colour was performed using a Datacolor- Microflash 200 Portable Spectrophotometer. The colour of the treated textiles was measured by placing the measuring sphere of the spectrophotometer onto the fabric.

To obtain a delta E (DE) measurement a standard (untreated) piece of dyed fabric was measured prior to measuring the colour of fabric which had been treated with fabric conditioners 1 or A.

**Table 3: Colour of fabric (knitted polyester) treated (by padding) with compositions 1 and A.**

| Sample | DE |
|---|---|
| A | **10.67** |
| 1 | **0.76** |

DE = Delta E, is commonly used to express colour change. The higher the DE, the bigger the colour change.

It will be seen that the polyester treated with the composition of the invention retained its deep red colour, whereas the polyester treated with composition 1 looked much lighter in comparison.

**Table 4: Colour of fabric (knitted polyester) treated with compositions 2 and B.**

| Sample | DE |
|---|---|
| B | **0.87** |
| 2 | **0.15** |

Again, the composition in accordance with the invention leads to a much smaller change in colour than the comparative example.

## CLAIMS

1. A fabric softening composition comprising a fabric softening compound and a switchable material capable of changing its hydrophobic-hydrophilic properties in response to an activation step, wherein the switchable material is present in an amount of from 0.1 to 50 wt %, based on the total weight of the composition and has a mean particle size of from 1 to 50 nm.

2. A fabric softening composition as claimed in claim 1 in which the switchable material is hydrophobic and becomes hydrophilic upon exposure to light, particularly UV light.

3. A fabric softening composition as claimed in claim 2 in which the switchable material is selected from ZnO and $TiO_2$.

4. A fabric softening composition as claimed in claim 1 in which the switchable material changes its hydrophobic-hydrophilic properties in response to change in pH, temperature change, heat flow, change in ionic strength or presence of an enzyme.

5. A composition as claimed in any preceding claim in which the fabric conditioning composition is selected from an oily sugar derivative, a cationic fabric softening compound and mixtures thereof.

6. A composition as claimed in claim 5 in which the cationic fabric softening compound is a quaternary ammonium compound having at least two $C_{12-28}$ groups connected to the nitrogen head group that may independently be alkyl or alkenyl groups, preferably being connected to the nitrogen head group by an ester link.

7. A composition as claimed in any preceding claim which additionally comprises one or more ingredients selected from perfume, non-ionic surfactant, fatty acid, fatty alcohol and viscosity modifier.

8. A composition as claimed in any preceding claim, wherein the switchable material is present in an amount of from 0.1 to 10 wt %, preferably from 0.1 to 5 wt % based on the total weight of the composition.

9. A composition as claimed in any preceding claim, wherein the switchable material has a mean particle size of from 1 to 10 nm.

10. A method of treating a dyed fabric having a colour, comprising rinsing the dyed fabric in a composition as defined in any one of claims 1 to 9, to deposit fabric conditioner and switchable material thereon, drying the fabric and before, after or simultaneously with the drying, subjecting a portion of the fabric to an activation step to cause the switchable material deposited in said portion to undergo a change in its hydrophobic-hydrophilic properties, wherein said method does not have a detrimental effect on the colour of the dyed fabric.

11. A method as claimed in claim 10 in which the switchable material is selected from ZnO and $TiO_2$ and the activation step comprises exposure to UV light.

12. A method as claimed in claim 10 or claim 11 in which one side or portion of the fabric is subjected to said activation step.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/075918

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/00 C11D3/12 C11D11/00 D06M11/44 D06M11/46
ADD.

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)
C11D D06M

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 practicable, 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 | JP 2005 082708 A (SOUSHIN KK)<br>31 March 2005 (2005-03-31)<br>the whole document | 1-3,5-12 |
| X | WO 2008/058831 A1 (UNILEVER PLC [GB];<br>UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN];<br>BOARDMAN) 22 May 2008 (2008-05-22)<br>cited in the application<br>the whole document | 1-12 |
| X | WO 2011/042275 A1 (UNILEVER PLC [GB];<br>UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN];<br>BOARDMAN) 14 April 2011 (2011-04-14)<br>the whole document | 1-3,5-12 |

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family 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 application or patent 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 | Date of mailing of the international search report |
|---|---|
| 20 March 2013 | 28/03/2013 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Neys, Patricia |

1

Form PCT/ISA/210 (second sheet) (April 2005)

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/075918

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO 2008/128827 A1 (HENKEL AG & CO KGAA [DE]; SCHRECKER SASCHA [DE]; MEINE GEORG [DE]) 30 October 2008 (2008-10-30)<br>claims 1-13<br>page 14, last paragraph - page 15, paragraph 5<br>page 3, paragraph 3 - page 7, paragraph 1 | 1-3,5-12 |
| X | WO 2006/097207 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]; DONEVA)<br>21 September 2006 (2006-09-21)<br>claims 1-6,10-14,21<br>examples<br>page 7, line 3 - page 8, line 22<br>page 10, line 30 - page 14, line 34 | 1-3,5-12 |
| X | US 6 774 096 B1 (PAYE MARC [BE])<br>10 August 2004 (2004-08-10)<br>claims 1,5<br>example<br>column 1, line 6 - line 11<br>column 8, line 40 - line 47 | 1-3,7-9 |
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