A composition comprises a microencapsulated thermochromic and/or photochromic material dispersed in a crosslinked polymer matrix. The polymer matrix may comprise acrylic and/or polyvinyl polymers and the thermochromic material may comprise a liquid crystal. Typically, the composition contains 10-50 vol.% of the polymer, 1-20 vol.% of the microencapsulated material, and 35-90 vol.% of water based on the total composition. A method of preparing the composition is also disclosed and comprises the steps of adding a microencapsulated thermochromic and/or photochromic material to a polymer and crosslinking the polymer to form a polymer matrix. A crosslinking agent and/or an initiator may be added in the crosslinking step, whilst water may be added to the polymer prior to the crosslinking step. A method of contacting a substrate, e.g. by immersion, with the composition is further claimed, wherein the substrate may comprise textile, wood, paper, tiles, metal or plastics.
A Thermochromic and/or Photochromic Composition

The present invention relates to a thermochromic and/or photochromic composition for dyeing a substrate, such as a textile. The present invention also relates to a method of preparing the thermochromic and/or photochromic composition, and to a method of treating a substrate with the composition.

Thermochromic and photochromic materials are known in the art. However, these materials tend to lack affinity with fibre and, as a result, cannot be applied directly to fabrics using conventional dyeing methods. Although thermochromic and photochromic materials have been applied to fabrics by printing, such methods rely on coating the surface of the fibre with a resin containing the dye, rather than impregnating the dye into the fibre. As a result, the printed fabrics tends to lose their colour after washing.

US 5,221,228 describes a method of dyeing a cellulose fibre textile product with thermochromic material and/or photochromic material. The method comprises treating a cellulose fibre textile product with a cationic compound, and then immersing the cationically treated textile product in a dispersion of thermochromic material and/or photochromic material. The thermochromic or photochromic materials are encapsulated in polymer microcapsules or contained in a polymer matrix, which bind(s) to the cationically treated textile product by physical adsorption and an ionic bond.
According to the first aspect of the present invention there is provided a thermochromic and/or photochromic composition comprising

(i) a microencapsulated thermochromic material
and/or a microencapsulated photochromic material; and
(ii) a cross-linked polymer matrix,
wherein the a microencapsulated thermochromic material and/or a microencapsulated photochromic material is dispersed within the polymer matrix.

According to another aspect of the present invention there is provided a method of preparing a composition as defined in any one of the preceding claims comprising the steps of

(i) providing a polymer;
(ii) adding a microencapsulated thermochromic material and/or a microencapsulated photochromic material to the polymer; and
(iii) cross-linking the polymer to form a polymer matrix.

The term "thermochromic composition" is used herein to describe a composition comprising a thermochromic material which allows a reversible colour change as a function of temperature change.

The term "photochromic composition" is used herein to describe a composition comprising a photochromic material which allows the reversible colour change as a function of the change in ultraviolet light.
The present invention will now be further described. In the following passages different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

Any suitable polymer may be used to form the polymer matrix. Preferred polymers are polymer compounds selected from the group consisting of acrylic polymers, polyvinyl acetate, polyvinyl alcohols, polyurea, polyamide, polyester, polyurethane, epoxy resin, urea resin, melamine resin, gelatine, ethyl cellulose and polystyrene. More preferably the polymer is an acrylic polymer or a polyvinyl polymer, such as polyvinyl acetate or polyvinyl alcohol. Most preferably, the polymer is an acrylic polymer.

Examples of suitable acrylic polymers are well known in the art, and can be prepared by polymerizing copolymerizable monomers with other, optionally functional group-containing monomers. Suitable copolymerizable copolymerization monomers include olefinic unsaturated monomers such as ethylene, propylene, and isobutylene, aromatic monomers such as styrene, vinyltoluene, esters of acrylic acid and methacrylic acid with alcohols having 1 to 18 carbon atoms such as methylacrylate, ethyl acrylate, ethylmethacrylate, theyl acrylate, ethyl methacrylate, propylacrylate, propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl
methacrylate, lauryl acrylate, and lauryl methacrylate, vinyl esters of carboxylic acids having 2 to 11 carbon atoms such as vinyl acetate, vinyl propionate and vinyl 2-ethylhexylacrylate and other common co-monomers such as vinyl chloride, acrylonitrile and methacrylonitrile.

Preferably the polymers of the present invention will be functionalised polymers, such that they are capable of being chemically bound to other polymers used in the present invention. It will be understood that the polymers may be functionalised with, for example, hydroxy, amino, epoxy, or carboxy groups.

The polymer used to form the polymer matrix is cross-linked. Without wishing to be bound by any theory, it is this cross-linked polymer network that is believed to retain or trap the microencapsulated thermochromic material and/or photochromic material in place, reducing the risk of these materials leaching out or separating from the remainder of the composition. By retaining or trapping the microencapsulated thermochromic and/or photochromic materials in this manner, the composition of the present invention may be used to dye substrates, such as textiles, in a satisfactory manner.

The polymer may be cross-linked using any suitable method. For example, a cross-linking agent or an initiator may be used.

Any suitable initiator may be used to initiate a cross-linking reaction between polymer strands. Examples of suitable initiators include peroxides, peresters and
persulfates. Initiators may be selected from a group consisting of, but not limited to, hydrogen peroxide, alkyl peroxides, substituted alkyl peroxides, aryl peroxides, substituted aryl peroxides, acyl peroxides, alkyl hydroperoxides, substituted alkyl hydroperoxides, aryl hydroperoxides, substituted aryl peroxides, heteroalkyl peroxides, substituted heteroalkyl peroxides, heteroalkyl hydroperoxides, substituted heteroalkyl hydroperoxides, heteroaryl peroxides, substituted heteroaryl peroxides, heteroaryl hydroperoxides, substitute heteroaryl hydroperoxides, alkyl peresters, substituted alkyl peresters, aryl peresters, substituted aryl peresters, persulfates, such as ammonium persulfate and potassium sulfate and azo compounds. Most preferred initiators include BPO and AIBN.

Initiators may also include ceric ions, for example in the form of ceric salts such as ceric nitrate, ceric sulphate, ceric ammonium nitrate, ceric ammonium sulphate.

Suitable initiators also include acids. Such acids include, but are not limited, hydrochloric acid, phosphoric acid, sulphuric acid, nitric acid, acetic acid, formic acid, oxalic acid, tartaric acid, monochloroacetic acid, dichloroacetic acid, and trichloroacetic acid.

In a preferred embodiment, the initiator is an ammonium salt, acesulfame K-acetic acid acetone nitrile, sodium metasulfite, hydrogen peroxide, sodium sulfoxylate, or mercapto benzthiozole-thiazone 2 MBS.
It may be advantageous for cross-linking to occur in the presence of a catalyst. Acid initiators, such as hydrochloric, phosphoric, sulphuric, nitric, acetic, formic, oxalic, tartaric, monochloroacetic, dichloroacetic, trichloroacetic and similar acids may function both as initiators and catalysts. When other forms of initiators are used, the presence of an additional catalyst may be desirable. Each of the acids mentioned above may function as a catalyst. In addition, well-known catalysts include bases such as potassium hydroxide and sodium hydroxide, and another recognised catalyst is ferrous sulphate.

Any suitable microencapsulated thermochromic materials may be used in the present invention. Suitable materials are well known in the art and are commercially available. Suitable microencapsulated thermochromic materials may, for example, be obtained from H.W. Sands Corporation, Siltex (Shanghai) Trading Co. Ltd., New Prismatic Enterprise (Taiwan) or Korchem Service Corporation. Preferably, the microencapsulated thermochromic material is a polymer microencapsulated thermochromic material. Examples of polymer microencapsulated thermochromic materials which are suitable for the present invention include Chromazone Inc.

The thermochromic material undergoes a thermochromic transition at a predefined temperature. In one embodiment, the thermochromic material changes from a substantially transparent or clear state to a coloured state (or vice-versa) at the predefined temperature. In another embodiment, the thermochromic material changes from one colour to another at the predefined temperature.
Mixtures of thermochromic materials may be employed.

In one embodiment, a thermochromic material having more than one activation temperature may be employed. For example, when a thermochromic material having two activation temperatures is used, the material undergoes two thermochromic transitions at two different predefined temperatures. The first thermochromic change may occur when the temperature of the thermochromic composition falls below the lower limit of the target temperature range and the second thermochromic change may occur when the temperature of the thermochromic composition exceeds the upper limit of the target temperature range. As a result of these thermochromic changes, the thermochromic composition will have a different visual appearance depending on whether the composition is within the target temperature range, above the target temperature range or below the target range. Thermochromic materials with three, four, five or more activation temperatures may be used.

Any suitable material that exhibits a thermochromic transition at a predefined temperature may be used as the thermochromic material. As mentioned above, the thermochromic material may change colour or change from a substantially transparent or clear state to a coloured state (or vice-versa) at a predefined temperature. Preferably, the thermochromic transition is reversible. Thus, the thermochromic transition observed when the temperature of the material exceeds a particular threshold is reversed when the temperature of the material falls below that threshold.
In one embodiment, the thermochromic material comprises a thermochromic composition comprising a) an electron donating colour-developing organic compound, b) an electron-accepting compound and c) a reaction medium. The reaction medium typically plays an important role in determining the temperature at which the colour-developing reaction between components a) and b) arises. Examples of thermochromic compositions of this type are described in US 4,957,949, US 6,468,088, US 4,028,118 and US 4,732,810.

The electron-donating colour-developing organic compound (a) may be a colourless compound that forms a coloured product upon reaction with the electron-accepting compound (b). Suitable electron-donating colour-developing organic compounds (a) include phenylmethanes, phthalides, phthalans, lactones, carbinols, auramines, lactams, indolines, spiropyran and fluorans. For example, diaryl phthalides, indolylphthalides, polyarylcarbinols, leuco-auramines, acylauramines, fluoran leuco compounds, triphenylmethane phthalide leuco compounds and lactam leuco compounds may be used.

Examples of compounds (a) include 3,3'-dimethoxyfluoran, 3-chloro-6-phenylaminofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethyl-7,8-benzofluoran, 3,3',3''-tris(p-dimethylaminophenyl)phthalide, 3,3'-bis(p-dimethylaminophenyl)-7-phenylaminofluoran and 3-diethylamino-6-methyl-7-phenylaminofluoran.

Other examples of compounds (a) include Crystal Violet lactone, Malachite Green lactone, Michler's hydrol, Crystal Violet carbinol, Malachite Green carbinol, N-(2,3-
dichlorophenyl)-leuco auramine, N-benzoyl auramine, N-acetyl
auramine, N-phenyl auramine, Rhodamine B lactam, 2-
(phenylimonoethylidene)-3,3-dimethyl-indoline, N,3,3-
trimethyl-indolinobenzo-spiropyran, 8'-methoxy-N,3,3-
trimethylindolino-spiropyran, 3-diethylamino-6-methyl-7-
chloro-fluoran, 3-diethylamino-7-methoxy-fluoran, 3-
dimethylamino-6-benzyl oxy-fluoran, 1,2-benzo-6-
diethylaminofluoran, 3,6-di-p-toluidino-4,5-dimethylfluoran-
phenylhydrazide-gamma-lactam, 3-amino-5-phenyl-8methyl-
fluoran, 2-methyl-3-amin o-6-methyl-7-methyl-fluoran, 2,3-
butylene-6-di-n-butylamino-fluoran, 3-diethylamino-7-
anilino-fluoran, 3-diethylamino-7-(p-toluidino)-fluoran, 7-
acetamino-3-diethylamino-fluoran, 2-bromo-6-cyclohexylamino-
fluoran and 2,7-dichloro-3-methyl-6-n-butylamino-fluoran.

Suitable electron-accepting compounds (b) include phenolic
compounds, such as phenolic hydroxyl compounds.
Monophenolic and polyphenolic compounds may be employed.
These may be substituted, for example, with alkyl, aryl,
acyl, alkoxy carbonyl and/or halogen atoms. Azoles, organic
acids, organic acids and organic salts may also be used.

Examples of suitable phenolic compounds include phenyl
phenol, bisphenol A, cresol, resorcinol, chlorolucinol, β-
naphthol, 1,5-dihydroxynaphthalene, pyrocatechol,
pyrogallol, trimer of p-chlorophenol-formaldehyde condensate
and the like.

Examples of azoles include ben zotri a zoles, such as 5-
chlorobenzotriazole, 4-laurlaminosulfobenzotriazole, 5-
butylbenzotriazole, dibenzotriazole, 2-oxybenzotriazole, 5-
ethoxycarbonyl-benzotriazole; imidazoles, such as oxybenzimidazole; tetrazoles and the like.

Examples of organic acids include aromatic carboxylic acids, aliphatic carboxylic acids and substituted derivatives thereof. Examples of aromatic carboxylic acids are salicylic acid, methylenebisalicylic acid, resorcylic acid, gallic acid, benzoic acid, p-oxybenzoic acid, pyromellitic acid, β-naphthoic acid, tannic acid, toluic acid, trimellitic acid, phthalic acid, terephthalic acid and anthramilic acid. Examples of aliphatic carboxylic acids include those containing about 1-20 carbon atoms, preferably about 3-15 carbon atoms, such as stearic acid, 1,2-hydroxystearic acid, tartaric acid, citric acid, oxalic acid and lanric acid. Examples of esters include alkyl esters of aromatic carboxylic acids in which the alkyl moiety has 1 to 6 carbon atoms, such as butyl gallate, ethyl p-hydroxybenzoate and methyl salicylate. Examples of salts include ammonium salt and metal salts of the above organic acids. The metal salts include, for example, lithium, sodium, calcium, magnesium, aluminium, zinc, tin, titanium, nickel or the like metal salts.

Other examples of electron-accepting compounds (b) include tert-butyl phenol, nonyl phenol, dodecyl phenol, styrenated phenol, 2,2'-methylene-bis(4-methyl-6-tert-butyl-phenol), alpha-naphthol, beta-naphthol, hydroquinone monomethyl ether, guaiacol, eugenol, p-chlorophenol, bromophenol, o-chlorophenol, o-bromophenol, o-phenylphenol, p-phenylphenol, p-(p-chlorophenyl)-phenol, o-(o-chlorophenyl)-phenol, methyl p-hydroxybenzoate, ethyl p-hydroxybenzoate, propyl p-hydroxybenzoate, octyl p-hydroxybenzoate, dodecyl phenol p-
hydroxybenzoate, 3-isopropyl-catechol, p-tert-butyl-catechol, 4,4'-methylene-diphenol 4,4'-thio-bis(6-tert-butyl-3-methyl-phenol), bisphenol A, 1,2-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, chlorocatechol, bromocatechol, 2,4-dihydroxybenzophenone, phenol, phthalein, o-cresol phthalein, methyl protocatechuate, ethyl protocarechuate, propyl protocatechuate, octyl protocatechuate, dodecyl protocatechuate, 2,4,6-trihydroxymethyl-benzene, methyl gallate, ethyl gallate, ethyl gallate, propyl gallate, butyl gallate, hexyl gallate, octyl gallate, dodecyl gallate, cetyl gallate, 2,3,5-trihydroraphthalene, tannic acid and phenol-formaldehyde prepolymers.

The reaction medium (c) may be an alcohol, such as an aliphatic monovalent alcohol. Preferably, the alcohol has more than 8 carbon atoms. More preferably, the alcohol has 10 to 30 carbon atoms, for example, 12 to 20 carbon atoms. Specific examples include fatty alcohols, such as lauril alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, docosyl alcohol and oleyl alcohol. Other examples include octyl alcohol and dodecyl alcohol.

The ratio of components a), b) and c) may be varied to suit requirements. Typically, the composition contains 1 to 50 weight %, preferably 5 to 20 weight % of component (a), 2 to 40 weight %, preferably, 5 to 30 weight % of component (b) and 10 to 90 weight %, preferably 20 to 60 weight % of component (c).

Components (a), (b) and (c) may be each a mixture of two or more compounds.
Optionally, the thermochromic composition may further comprise an alcohol ester (d). Suitable alcohol ester components include octyl caprylate, decyl caprylate, octyl caprate, decyl caprate, cetyl caprate, stearyl caprate, butyl laurate, octyl laurate, lauryl laurate, stearyl laurate, butyl myristate, decyl myristate, myristyl myristate, cetyl myristate, octyl palmitate, butyl stearate, decyl stearate, lauryl stearate, stearyl stearate, 12-hydroxy stearic acid triglyceride and the like. The alcohol ester component may affect the sharpness and temperature of the colouration reaction. Component d) may optionally be present in an amount of 1 to 10 weight % of the composition.

The thermochromic composition of the present invention is microencapsulated prior to use. Any coating material may be used to microencapsulate the composition. Examples include polyurea, polyamide, polyurethane, polyester, epoxy resin, melamine resin, urea resin, methylcellulose, carboxymethylcellulose, cationized starch, carboxymethylated starch, ethylcellulose, polystyrene, polyvinyl acetate, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylic acid, polyacrylamides and polymers and copolymers of maleic acid. Other examples of coating materials include alginic acid and salts thereof, carrageenan, pectin and gelatin.

The microcapsules may be prepared by any suitable method. Examples include interfacial polymerization, in-situ polymerization, submerged hardening, coating, phase separation from an aqueous solution, phase separation from an organic solvent, melt dispersion cooling, air suspension coating and spray drying.
The microcapsules may have a particle diameter of from 0.01 to 150 μm, preferably from 0.01 to 100 μm, more preferably from 0.01 to 50 μm and yet more preferably 0.01 to 30 μm.

The microencapsulated thermochromic material may be formulated as an ink, paint or dye before being used in the composition of the present invention. Alternatively, the thermochromic material may be employed in crystal form. Preferably, the thermochromic material of the present invention is in the form of a liquid crystal.

The thermochromic material(s) may undergo a thermochromic transition(s) at a temperature from -60 to +60°C, preferably from 0 to +50°C. Within this range, the transition(s) may occur at a temperature from 10 to 50°C, preferably 15 to 45°C, for example, 20 to 40°C.

When the thermochromic composition is applied to clothing, the thermochromic material may be chosen such that a change in colour occurs over the temperature range of from 20°C to 40°C, more preferably from between 30 °C to 38 °C, most preferably from between 35 °C to 37 °C. In this embodiment, the thermochromic material may change colour depending on the temperature of the user's body. Accordingly, different areas of the item of clothing may take on a different appearance.

Any suitable microencapsulated photochromic material may be used in the present invention. The photochromic materials of the present invention are microencapsulated, preferably polymer microencapsulated. Commercially available polymer
microencapsulated photochromic material may be used in the present invention. Suitable microencapsulated photochromic material may, for example, be obtained from Nae Woi Korea Ltd.; New Prismatic Enterprise, or Siltex (Shanghai) Trading Co. Ltd.

The microencapsulated photochromic materials may be obtained by microencapsulating an organic photochromic material using methods known in the art. Examples of the organic photochromic compound include azobenzene compounds, thioindigo compounds, dithizone metal complexes,Spiroopyran compounds, spirooxazine compounds, naphthopyran compounds, fulgide compounds, dihydropyrene compounds, spirothiopyran compounds, 1,4-WH-oxazine, triphenylmethane compounds and violegen compounds.

Examples of specific organic photochromic compounds include 1,3,3-trimethylspiro(indolino-2,3'-(3H)naphtha(2,1-b)(1,4)-oxazine), 5-methoxy-1,3,3-trimethylspiro(indolino-2,3'(3H)naphton(2,1-b)(1,4)-oxazine), 5-chloro-1,3,3-trimethylspiro(indolino-2,3'(3H)naphtha(2,1-b)(1,4)-oxazine), 8'-piperidono-1,3,3-trimethylspiro(indolino-2,3'(3H)naphtha(2,1-b)(1,4)-oxazine), 1-benzyl-3,3-dimethylspiro(indolino-2,3'(3H)naphtha(2,1-b)(1,4)-oxazine), 1,3,5,6-tetramethyl-3-ethylspiro(indolino-2,3'(3H)naphtha(2,1-b)(1,4)-oxazine), 1,3,3,5,6-pentamethylspiro(indolino-2,3'(3H)naphtho(2,1-b)(1,4)-oxazine), 1,3',3'-trimethylspiro(2H-1-benzopyran-2,2'-indolino), 3,3,1-diphenyl-3H-naphtho-(2,1-13)pyran, 1,3,3-triphenylspiro(indolino-2,3'(3H)naphto(2,1-b)pyran), 1-(2,3,4,5,6-pentamethylbenzyl)-3,3-dimethylspiro(indolino-2,3'(3H)naphtho(2,1-b)pyran), 1-(2-nitrobenzyl)-3,3-
dimethylspiro(indolino-2,3'-(3H)-naphtho(2,1-b)pyran), 1,1-
diphenynaphthopyran, 2,5-dimethylfuryl-trimethylfulgide and
2-methyl-5-chlorotrimethylfulgide.

5 Preferably the microencapsulated photochromic materials have
an average size of less than 150 µm, more preferably, less
than 100 µm, and most preferably less than 50 µm.

Preferably, the microencapsulated thermochromic material and
/or microencapsulated photochromic material is evenly
dispersed throughout the polymer matrix, so that substrates
may be evenly coated with these materials.

The thermochromic and/or photochromic composition described
above may include water. When the composition of the
present invention comprises water, the composition may be in
the form of an aqueous solution, suspension, colloidal
solution, emulsion or other physical aggregation.
Surfactants and/or emulsifiers may also be included in the
composition.

Preferably, the composition of the present invention
comprises polymer in an amount of 5 to 70% by volume,
preferably from 10 to 50% by volume, more preferably from 20
to 40% by volume of the total composition.

Preferably, the composition of the present invention
comprises microencapsulated thermochromic materials and/or
microencapsulated photochromic materials in an amount of
from 1 to 50% by volume, preferably from 1 to 20% by volume,
more preferably from 1 to 10% by volume of the total
composition.
Preferably, water comprises from 0 to 98% by volume, preferably 10 to 95% by volume, preferably from 20 to 90% by volume, more preferably from 35 to 90% by volume of the total composition.

When the composition of the present invention comprises water, water may be added to the composition before cross-linking the polymer to form a polymer matrix. Alternatively, or additionally, water may be added during, or after the cross-linking step.

According to a further aspect of the present invention, there is provided a method of treating a substrate comprising contacting the substrate with a composition as described above.

Preferably when substrate is treated using the method of the present invention, the substrate is at least partially immersed in said thermochromic and/or photochromic composition. Furthermore, the substrate may be agitated during immersion in said thermochromic and/or photochromic composition.

It is possible that the composition of the present invention may be impregnated into or onto the substrate by spraying, padding, dipping, painting or other means. It is preferable, in the case of textile, to immerse the textile in a bath containing the composition.

Uniform dispersion may be preferred. The time necessary to obtain uniform dispersion and attachment of the
thermochromic and/or photochromic composition to the substrate will vary with the particular method of contacting the composition onto the substrate.

5 Preferably, the method of treating the substrate as described herein further comprises a drying step, wherein after treatment of the substrate with the composition, the substrate is dried at room temperature. Preferably no additional heat is applied to dry the substrate.

10 The substrate may comprise textile, plastic, metal, plaster, wall surfaces, paper, tiles and wood. Preferably, the substrate is a textile, such as a natural and/or synthetic textile.

15 It will be understood that a number of textiles may be dyed using the thermochromic and/or photochromic composition of the present invention. The textile may be a synthetic and/or natural textile. The textile may comprise polyester, polyamides, polyvinyl alcohols, lyocell, rayon, viscose, nylon, cotton, linen, flax, hemp, jute and wool, acetates, acrylic, elastane, silk, cotton fibres, polyester fibres, polyamide fibres, acrylic fibres, wool fibres, silk fibres, linen fibres, synthetic fibres, semi-synthetic fibres, natural fibres, viscose fibres, elastane fibres or a combination thereof. In particular, denim may be dyed using the method of the present invention.

The textile may be in the form of clothing, for example T-shirts; trousers, such as jeans; underwear, such as pants, socks, bras; jackets; blouses; shirts; skirts; dresses;
coats; scarves; gloves; ties; boots; shoes; clothing
accessories and hair accessories.

In one embodiment of the present invention, the composition
comprising thermochromic material is applied to a pair of
jeans, for example white jeans. The thermochromic material
is chosen such that the colour change occurs at
approximately 35 °C, so that when the material of the jeans
is above 35 °C a colour change may be observed, for example
from blue to white. When the jeans are at a temperature of
less than 35°C, the jeans appear blue.

It will be understood by those skilled in the art that, when
textile impregnated with the composition of the present
invention is worn, not all of the textile will change colour
at the same time. Parts of the textile in close contact
with the wearer are likely to heat up before parts not in
close contact with the wearer. These warmer areas will
generally change colour before cooler areas. Creased areas
of the textile may also be at a different temperature to
unch creased areas of the textile. In the case of a pair of
jeans, for example, uncreased areas of the jeans may be of a
different colour to creased areas of the jeans.

It will be understood that the composition of the present
invention may be applied to the whole or part of the
substrate.

The composition of the present invention may be used to
colour substrates, such as textiles, in a satisfactory
manner. Preferably, the composition of the present
invention may be applied directly to the substrate, and pre-
treatment steps, such as cationic pre-treatment steps are not necessary. Without wishing to be bound by any theory, it is believed that the composition forms a physical bond with the substrate. The thermochromic and/or photochromic materials are believed to be retained in the cross-linked polymer matrix, such that they are prevented from leaching out or separating from the remainder of the composition.

According to a further aspect of the present invention, there is provided a substrate treated by the method as described herein.

Preferably, the substrate is a textile. The treated textile product obtained by the process of the present invention contains an high density of thermochromic and/or photochromic material compared to textiles dyed using conventional dyeing methods. Furthermore, it maintains a good texture, soft handling touch and it has excellent colour fastness to rubbing and colour fastness to washing.

The following examples further illustrate the present invention.

The microencapsulated thermochromic materials used in Examples 1 to 5 are commercially available from Chromazone, Inc.
Example 1

A thermochromic composition was prepared from the following constituents (percentages are percentage weight by volume):
63% water
17% acrylic polymer
10% thermochromic microcapsules
10% hydrogen peroxide.

2 litres of the thermochromic composition of the present invention were made in the following way.
1.26 litres of water was added to a bowl, followed by 0.34 litres of acrylic polymer. 0.20 litres of thermochromic microcapsules were then added to the mixture, which was thoroughly stirred. The mixture was then checked for desirability of colour. 0.20 litres of hydrogen peroxide was then added to the mixture and mixed in.

Method of dyeing jeans
The pair of white jeans was then fully immersed into the dye. The jeans were 'stirred' in the dye for 5 minutes to ensure that the dye fully impregnated the denim. The denim was left immersed in the dye for a further 10 minutes. The jeans were then taken out of the dye and hung to dry at room temperature.
Example 2

A thermochromic composition was prepared from the following constituents (percentages are percentage weight by volume):

- 67.3% water
- 26.5% acrylic polymer
- 2.2% thermochromic microcapsules
- 4% hydrogen peroxide.

446ml of the thermochromic composition of the present invention were made in the following way.

300 ml of water was added to a bowl. 118ml of acrylic polymer was to the water, followed by 10ml of thermochromic microcapsules. The mixture was then thoroughly stirred and checked for desirability of colour. 18ml of hydrogen peroxide was added to the mixture and stirred in.

Method for painting a piece of pine wood.
The dye was applied to a piece of pinewood using a paint brush, in the conventional way. The wood was then left to dry at room temperature.

Example 3

A thermochromic composition was prepared from the following constituents (percentages are percentage weight by volume):

- 72% water
- 22% acrylic polymer
- 2% thermochromic microcapsules
- 4% hydrogen peroxide.
446 ml of the thermochromic composition of the present invention were made in the following way. 321 ml of water was added to a bowl, followed by 98ml of acrylic polymer. To this mixture, 9ml of thermochromic microcapsules was added. The mixture was thoroughly stirred and then checked for desirability of colour. 18ml of hydrogen peroxide was then added to the mixture and stirred in.

Method for spraying a piece of pig suede leather
The thermochromic spray paint described above was then placed into a manually air pressurised spray gun. A leather piece was then sprayed on the suede side and left to dry at room temperature.

Example 4

A thermochromic composition was prepared using the method described is Example 3.

Method for dyeing the fur of a long hair Toskana pelt.
A sponge was dipped into the mixture. The fur side of a piece of Toskana sheepskin was "dabbed" with the sponge. The above process was continued until the fur was covered with the dye completely. The Toskana was left to dry.

It was found that some of the fur had adhered to surrounding fur. The Toskana was "brushed" with a hair brush which returned the Toskana fur to its original condition and left the dye intact to the fur.
Example 5

A thermochromic composition was prepared from the following constituents (percentages are percentage weight by volume):

- 70% water;
- 18% Hycar 261475 emulsion (T. M. Noveon), a non-ionic crosslinkable acrylic copolymer emulsion;
- 9% thermochromic microcapsules;
- 3% SC100 catalyst and cross-linker (Shanghai Secure Trading Co.)

The thermochromic composition was made using the relative percentages given above. Water was placed in a bowl, followed by the acrylic co-polymer. To this mixture, the thermochromic microcapsules were added. The mixture was thoroughly stirred and then checked for desirability of colour. The cross-linker was then added to the mixture and stirred in.
1. A thermochromic and/or photochromic composition comprising
   (i) a microencapsulated thermochromic material
       and/or a microencapsulated photochromic material; and
   (ii) a cross-linked polymer matrix,
wherein the a microencapsulated thermochromic material and/or a microencapsulated photochromic material is dispersed within the polymer matrix.

2. A composition as defined in claim 1 further comprising water.

3. A composition as defined in claim 1 or claim 2 wherein the polymer matrix comprises acrylic and/or polyvinyl polymers.

4. A composition as defined in any one of the preceding claims comprising a thermochromic material which comprises a liquid crystal.

5. A composition as defined in any one of the preceding claims wherein the percentage of polymer is from 10 to 50% by volume of the total composition.

6. A composition as defined in any one of the preceding claims wherein the percentage of the microencapsulated thermochromic material and/or the microencapsulated
photochromic material is from 1 to 20% by volume of the total composition.

7. A composition as defined in any one of claims 2 to 6 wherein the percentage of water is from 35 to 90% by volume of the total composition.

8. A method of preparing a composition as defined in any one of the preceding claims comprising the steps of
   (i) providing a polymer;
   (ii) adding a microencapsulated thermochromic material and/or a microencapsulated photochromic material to the polymer; and
   (iii) cross-linking the polymer to form a polymer matrix.

9. A method as defined in claim 8 further comprising adding water.

10. A method as defined in claim 9 wherein the water is added to the polymer before the cross-linking step.

11. A method as defined in any one of claims 8 to 10 wherein a cross-linking agent and/or an initiator is added in the cross-linking step.

12. A method as defined in any one of claims 8 to 11 wherein steps (i) and (ii) are performed before step (iii).
13. A method of treating a substrate comprising contacting the substrate with a composition as defined in any one of claims 1 to 7.

14. A method as defined in claim 13 wherein the substrate comprises textile, wood, paper, tiles, metal or plastic.

15. A method as defined in claim 13 or 14 wherein the substrate is at least partially immersed in said composition.

16. A method as defined in claim 15 wherein the substrate is agitated during immersion in said composition.

17. A method as defined in any one of claims 13 to 16 wherein after treatment of the substrate with the composition, the substrate is dried at room temperature.

18. The substrate treated by the method of any one of claims 13 to 17.

19. The substrate of claim 18, which is a garment.

20. A thermochromic and/or photochromic composition as substantially and hereby described with reference to any one of the examples.

21. A method of preparing a composition as substantially and hereby described with reference to any one of the examples.
22. A method of treating a substrate as substantially and hereby described with reference to any one of the examples.
Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

<table>
<thead>
<tr>
<th>Category</th>
<th>Relevant to claims</th>
<th>Identity of document and passage or figure of particular relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>1-4,8-19</td>
<td>EP 0564959 A1 (MERCK) see particularly line 10, page 1, lines 10-11 &amp; 19-21, page 2, lines 16-17 &amp; 22, page 6, and claims 1, 4, 7 &amp; 12.</td>
</tr>
<tr>
<td>X</td>
<td>1-4,8-10,12-19</td>
<td>WO 90/02054 A1 (WILLMORE) see particularly lines 21-24, page 3, lines 11-14 &amp; 24, page 6, Example and claims 1, 5, 10 &amp; 14-18.</td>
</tr>
<tr>
<td>X</td>
<td>1-4,8-10,12-18</td>
<td>EP 0357844 A1 (AKZO) see particularly lines 51-55, page 3 and claims 1-2.</td>
</tr>
<tr>
<td>X</td>
<td>1-3,8-14,17-19</td>
<td>GB 2270321 A (MATSUMI SHIKISO) see particularly lines 3-5, page 18, line 21, page 18 to line 4, page 19, Examples, and claims 6-7.</td>
</tr>
<tr>
<td>X</td>
<td>1-3,13-18</td>
<td>EP 1211299 A2 (THE PILOT INK CO) see particularly paragraphs [0005], [0026], and [0027].</td>
</tr>
<tr>
<td>X</td>
<td>1,3,13-18</td>
<td>US 4826550 A (SHIMIZU et al) see particularly lines 12-18, column 3, Example 5, and claim 1.</td>
</tr>
</tbody>
</table>

Categories:
- X Document indicating lack of novelty or inventive step
- Y Document indicating lack of inventive step if combined with one or more other documents of the same category.
- & Member of the same patent family
- A Document indicating technological background and/or state of the art.
- P Document published on or after the declared priority date but before the filing date of this invention.
- E Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:
Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:

Worldwide search of patent documents classified in the following areas of the IPC
C08K; C08L; C09D; C09K

The following online and other databases have been used in the preparation of this search report
WPI, EPODOC