Dyeing method and dyed product.

A dyeing method comprising:
a process of treating a cellulose fiber textile product with cationic compound; and
another process of treating the thus-treated textile product by immersing it in a dispersion containing reversibly
color changeable fine particles which involve thermochromic or photochromic material in high polymer com-
pond.
The present invention relates to a method of dyeing a cellulose fiber textile product with reversibly color changeable fine particles which involve thermochromic or photochromic material and a dyed product.

Three-component mixture of acid developing substance, acidic substance and solvent; two-component mixture of acid developing substance and acidic substance; cholesteric liquid crystals and metal complex salt crystals have been known as a kind of thermochromic material which shows reversible color changes as the temperature changes.

The three-component mixtures offer diverse colors and high coloring densities and change dramatically between colored and colorless states. The two-component mixtures offer higher coloring densities in comparison with the three-component mixtures. But the two-component mixtures change their colors relatively slowly and few of the mixtures show color changes in ordinary thermal circumstances. The cholesteric liquid crystals are capable of changing their colors to red, yellow, green, blue, violet and so on sensitively in arbitrary range of temperature. But they need black ground and offer lower coloring densities in comparison with the three-component mixtures. Excellent color changing function of these three-component mixtures, two-component mixtures and cholesteric liquid crystals is obtained only in cases where their components form a system at a strictly constant ratio. In order to keep their function, they are used in fine particle form which contains them in synthetic resin matrix or microcapsule form which contains them.

Many of metal complex salt crystals are not suitable for applying on textile product because of their toxicity.

With respect to photochromic materials which show reversible color changes in the presence or absence of light, a wide variety of organic photochromic compounds have been developed which show more sensitive color changes between colored and colorless states, which offer more diverse colors and which are more compatible with various organic compounds such as synthetic resins in comparison with conventional inorganic photochromic compounds such as silver halides.

Such organic photochromic compounds are used, for example, as dispersion in appropriate medium or in the form of microcapsule containing the dispersion.

None of these reversibly color changeable fine particles, i.e. particles of matrix or microcapsules which show reversible color changes by temperature or light are capable of directly dyeing fiber because of a lack of affinity with fiber. Although dyeing is possible by the synthetic resin printing method, the synthetic resin padding method and other methods using an adhesive such as synthetic resin binder, the coloring density obtained with reversibly color changeable fine particles involving thermochromic material or photochromic material is extremely lower than that obtained with an ordinary coloring agent. For example, in the case of the synthetic resin printing method, a fair coloring density is obtained only when bulky printing is conducted on a textile product using an ink containing such fine particles and synthetic resin binder at high concentrations. In this case, the surface of the textile product loses its fiber texture, its appearance worsens, and its color fastness to rubbing and color fastness to washing are insufficient. For these reasons, even when the entire surface of the cloth is colored, no commercially valuable product will be obtained. Therefore, it is the conventional practice to make patterns such as one-point patterns on a very narrow area on the cloth.

Also, when using the pigment resin padding method with high concentrations of reversibly color changeable fine particles and synthetic resin binder, these fine particles are not capable of being thoroughly adsorbed because of a lack of substantivity with fiber, and physical adhesion as in the pigment resin printing method cannot be expected; therefore, nothing more than extremely low coloring density can be obtained. Moreover, the obtained fiber texture, appearance, color fastness to rubbing, and other properties are insufficient.

It is an object of the present invention to provide a dyeing method which permits dyeing of a cellulose fiber textile product with reversibly color changeable fine particles which involve thermochromic or photochromic material in high densities which could not be obtained by any conventional method and which thus provides incomparably distinct colors upon their color development with no influence on the texture, appearance or other textile product properties.

It is another object of the invention to provide dyed product which is dyed with reversibly color changeable fine particles to high densities which could not be obtained formerly with no influence on the texture, appearance or other textile product properties.

The object described above can be accomplished by the dyeing method of the present invention, which comprises:

a process of treating a cellulose fiber textile product with cationic compound; and
another process of treating the thus-treated textile product by immersing it in a dispersion containing reversibly color changeable fine particles which involve thermochromic or photochromic material in high
The dyed product of the present invention is cellulose fiber textile product pretreated with cationic compound and dyed with reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound.

Cellulose fiber

Examples of the cellulose fiber for the present invention include natural fibers such as cotton and hemp and regenerated fibers such as rayon and cupra.

Cellulose fiber textile product

Examples of the cellulose fiber textile product described above include cellulose fiber yarns, blended yarns of cellulose fiber with polyester fiber, acrylic fiber, wool, etc., or fabrics or knits comprising cellulose fiber yarn and/or the blended yarn described above, cellulose-containing nonwoven fabrics, and sewn products such as apparels based on these fabrics, knits or nonwoven fabrics. Examples of sewn products are T-shirt, trainer, jumper, pants, jeans, socks, bag, cap, hat and so on.

The textile product for the present invention may be colored in advance.

Cationic compound

Examples of the cationic compound described above include quaternary ammonium salt type compounds, pyridinium salt type compounds, dicyandiamide type compounds, polyamine type compounds and polycation type compounds.

Specific examples of the cationic compounds are as follows.

Examples of the quaternary ammonium salt type compounds include quaternary ammonium salt type cationic surfactants such as trimethyloctadecylammonium chloride, trimethylhexadecylammonium chloride, trimethylundecylammonium chloride, trimethylhexylammonium chloride, laurylmethylhexylammonium chloride, lauryldimethylbenzylammonium chloride, dilauryldimethylammonium chloride, lauryltrimethylammonium chloride, alkylbenzyltrimethylammonium chloride, stearylbenzyltrimethylammonium chloride, and alkyltrimethylammonium chloride;

Examples of the pyridinium salt type surfactant such as laurylpyridinium chloride and stearylamine methylpyridinium chloride;

2,3-epoxypropyltrimethylammonium chloride;

3-chloro-2-hydroxypropyltrimethylammonium chloride;

Examples of the dicyandiamide type compounds include formaldehyde condensation product of dicyanamide.

Examples of the polyamine type include guanidine derivative condensation product of polyalkylpolyamine; polyethyleneimines and polyamidoamines.

disclosed in Unexamined Japanese Patent Publication No. 128382/1981; the polymer comprising the following monomer unit:

$$\begin{align*}
\text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2 \\
\text{H}_2 \text{C} \quad \text{N} \\
\text{CH}_2 \quad \text{CH}_3
\end{align*}$$

(SHALLOL DC (trade name) series, product of Dai-ichi Kogyo Seiyaku Co., Ltd.) and copolymers of quaternary ammonium salts and other vinyl polymers.

Of these cationic compounds, polyamine type compounds, dicyandiamide type compounds and quaternary ammonium salt type polymers and copolymers of quaternary ammonium salts and other vinyl monomers of polycation type are particularly effective in the present invention.

**Thermochromic material**

Examples of thermochromic materials available for the present invention include three-component mixture of acid developing substance, acidic substance and solvent; two-component mixture of acid developing substance and acidic substance; cholesteric liquid crystal and metal complex salt.

**Three-component mixture, two-component mixture**

Examples of the acid developing substance of three-component mixture and two-component mixture include triphenylmethanephthalide compounds, phthalide compounds, phthalan compounds, Acryl Leucomethylene Blue compounds, fluoran compounds, triphenylmethane compounds, diphenylmethane compounds and spiropyan compounds. More specific examples thereof include 3,6-dimethoxyfluoran, 3,6-dibutoxyfluoran, 3-diethylamino-6,8-dimethylfluoran, 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)phthalide, 3-diethylamino-7-phenylaminofluoran, 3,3-bis(p-diethylaminophenyl)-6-dimethylamino phthalide, 3-4(diethyaminophenyl)-3-(1-ethyl-2-methylindol-3-yl)phthalide, 3-(4-diethylamino-2-methyl)phenyl-3-(1,2-dimethylindol-3-yl)phthalide and 2''-(2-chloroanilino)-6''-dibutylaminospiro[phthalide-3,9'-xanthen].

Examples of the acidic substance of three-component mixture and two-component mixture include 1,2,3-benzotriazoles, phenols, thiourea derivatives and oxy aromatic carboxylic acids. More specific examples thereof include 5-butybenzotriazole, bissenzotriazole-5-methane, phenol, nonylphenol, bisphenol A, bisphenol F, 2,2''-bisphenol, 6 -naphthol, 1,5-dihydroxynaphthalene, alkyl p-hydroxybenzoate and phenol resin oligomers.

Examples of the solvent of three-component mixture and two-component mixture include alcohols, alcohol-acrylonitrile addsucts, azomethines and esters. More specific examples thereof include decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, beheny alcohol, lauryl alcohol-acrylonitrile addsucts, myristyl alcohol-acrylonitrile addsucts, stearyl alcohol-acrylonitrile addsucts, benzylidene-p-toluidine, benzylidene-butyramine, octyl caprylate, decyl caprylate, myristyl caprylate, decyl laurate, lauryl laurate, myristyl laurate, decyl myristate, lauryl myristate, cetyl myristate, lauryl palmitate, cetyl palmitate, stearyl
palmitate, cetyl p-t-butylbenzoate, stearyl 4-methoxybenzoate, dilauryl thiodipropionate, dimyristyl-
thiodipropionate, stearyl benzoate, benzyl stearate, benzyl thiodipropionbenzoate, diesteryl thiodipropionate
and benzyltrilaurate benzoate.

Cholesteric liquid crystal

Examples of the cholesteric liquid crystals include a composition of two or more kinds selected from
cholesterol acetate, cholesterol benzoate, cholesterol nonanate, cholesterol propionate, cholesterol oleyl
carbonate and cholesterol chloride.

Metal complex salt

Examples of the metal complex salt include complex compounds of silver, mercury, iodine or copper
and thiodicarbamic acid derivative complexes.

Photochromic material

Examples of the photochromic material usable for the present invention include azobenzene com-
ounds, thiindigo compounds, dithiozine metal complexes, spiropyran compounds, spirooxazine com-
ounds, fulgide compounds, dihydroprene compounds, spirothiopyran compounds, 1,4,2H-oxazine,
triphenylmethane compounds, viologen compounds, naphthopyran compounds, with preference given to
spiropyran compounds, spirooxazine compounds, fulgide compounds and naphthopyran compounds for the
dyeing method of the present invention.

Specific examples of photochromic material include 1,3,3-trimethylspiro[indoline-2,3'- (3H)naphtho(2,1-
b)](1,4)-oxazine,
6'-indolino-1,3,3-trimethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)(1,4)-oxazine],
5-chloro-1,3,3-trimethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)(1,4)-oxazine],
6'-piperidino-1,3,3-trimethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)(1,4)-oxazine],
1-benzyl-3,3-dimethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)(1,4)-oxazine],
1,3,5,6-tetramethyl-3-ethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)(1,4)-oxazine],
1,3,3,5,6-pentamethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)(1,4)-oxazine],
1,3,5,6-tetramethyl-3-ethylspiro[indoline-2,3'- (3H)pyrido(3,2-f)/(1,4)-benzooxazine],
1,3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline],
1,3,3-triphenylspiro[indoline-2,3'- (3H)naphtho(2,1-b)pyran],
1-(2,3,4,5,6-pentamethylbenzyl)-3,3-dimethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)pyran],
1-(2-nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'- (3H)naphtho(2,1-b)pyran],
2,2-diphenyl-naphtho(2,1-b)pyran,
2,2-di(p-methoxyphenyl)naphtho(2,1-b)pyran,
2,5-dimethylfuryl-trimethylfulgide and

Reversibly color changeable fine particles

Reversibly color changeable fine particles involve thermochromic or photochromic material in high
polymer compound.

Examples of the reversibly color changeable fine particles include particles containing thermochromic
material in high polymer microcapsules, particles containing dispersed thermochromic material in matrix of
synthetic resin, particles containing dispersed organic photochromic substance in matrix of synthetic resin,
particles containing dispersed organic photochromic substance in matrix of synthetic resin encapsulated in
high polymer microcapsules and particles containing dissolved or dispersed organic photochromic sub-
stance in medium encapsulated in high polymer microcapsules. It is preferable that the diameters of the
reversibly color changeable fine particles do not exceed 50 μm. If the diameters exceed 50 μm, exhaustion
of the particles into a cellulose fiber textile product often goes badly.

Thermochromic microcapsule

The three-component mixture, the two-component mixture or the cholesteric liquid crystals as ther-
nochomeric material can be microcapsules by, for example, the following method.
Microcapsules of 1 - 50 μm in diameter containing thermochromic material which are dispersed in aqueous dispersion can be obtained by carrying out a known encapsulation method such as the interfacial polymerization method, the insight polymerization method, the coacervation method, atmospheric suspension method or the interfacial precipitation method in water on thermochromic material selected from the above three-component mixture, the above two-component mixture and the above cholesteric liquid crystals and high polymer compound as coat former with surfactant, a protective colloid, a pH regulator, an electrolyte and other substances as needed.

The layers of the microcapsules can be plural by carrying out one or more kind of these encapsulation methods two or more times repeatedly.

Examples of preferable coat formers include polyisocyanate and polyamine for forming polyurea coat, polybasic acid chloride and polyamine for forming polyamide coat, polyisocyanate and polyhydroxy compound for forming polyurethane coat, epoxy compound and polyamine for forming epoxy resin coat, melamine-formaldehyde prepolymer for forming melamine resin coat, urea-formaldehyde prepolymer for forming urea resin coat, ethyl cellulose, polystyrene and polyvinyl acetate, and anionic high polymer compounds and amphoteric high polymer compounds described later.

It is preferable that the coat for the microcapsule described above be thermosetting because of excellent heat resistance.

Examples of preferably usable surfactants and protective colloids include anionid surfactants, amphoteric surfactants, anionic high polymer compounds, amphoteric high polymer compounds. In addition, nonionic surfactants can be used with these.

Usual electrolytes and pH regulators used in above capsulation methods are usable.

Examples of the anionic polymer compound described above include polyacrylic acid, poly-α-hydroxyacrylic acid, methacrylic acid, copolymers of these substances with other vinyl polymers, ethylene/maleic anhydride copolymer, butylene/maleic anhydride copolymer, vinyl ether/maleic anhydride copolymer, anion-modified polyvinyl alcohol, gum arabic, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and starch derivatives.

Examples of the amphoteris polymer compound described above include gelatin and casein.

Examples of the nonionic surfactant described above include polyoxyethylene alkyl ether, polyoxyethylenealkylalcohol ether and other polyoxyethylene derivatives, polyoxyethylene-polyoxypropylene block copolymer, aliphatic esters of sorbitan, fatty acid esters of polyoxyethylenesorbitol and fatty acid esters of glycerol.

Fine particle of thermochromic matrix

Particles containing dispersed three-component mixture, two-component mixture or cholesteric liquid crystals as thermochromic material in matrix of synthetic resin can be prepared by, for example, the following method.

Thermochromic material selected from the above and synthetic resin are first molten under heating conditions. The mixture is stirred until the thermochromic material is dispersed in the synthetic resin. The dispersion mixture is added to water containing surfactant and/or protective colloid with stirring the water to yield particles containing dispersed thermochromic material in matrix of synthetic resin.

Thermochromic material selected from the above and synthetic resin are first molten under heating conditions. The mixture is stirred until the thermochromic material is dispersed in the synthetic resin. The dispersion mixture is frozen and pulverized to give particles containing dispersed thermochromic material in matrix of synthetic resin.

Examples of the synthetic resin described above include acrylic polymers such as polyvinyl butyral,
polyvinyl alcohol and polymethacrylate; styrene polymers such as polystyrene and ABS resin; polyester polymers such as polycarbonate; polyether polymers such as polyethylene oxide; polyolefin polymers such as polyethylene and polypropylene, ethyl cellulose, polyvinyl acetate, polyvinyl chloride, melamine resin, epoxy resin and polyurethane resin.

It is possible to add ultraviolet absorber, ultraviolet stabilizer, antioxidant, antireductant, surfactant, fluorescent brightening agent and so on to the above thermochromic microcapsules or fine particles of thermochromic matrix as needed.

Fine particles of photochromic matrix

Particles containing dispersed organic photochromic substance as photochromic material in matrix of synthetic resin can be prepared, for example, in a similar manner as the above method of preparing fine particle of thermochromic matrix with use of similar synthetic resin.

Photochromic microcapsule

Particles containing dispersed organic photochromic substance in matrix of synthetic resin encapsulated in high polymer microcapsules or particles containing solved or dispersed organic photochromic substance in medium encapsulated in high polymer microcapsules can be prepared, for example, in a similar manner as microcapsulation of thermochromic material except that organic photochromic substance dispersed in matrix of synthetic resin or organic photochromic substance solved or dispersed in medium is used in place of thermochromic material.

The medium is preferably high boiling solvent, plasticizer, synthetic resin, hindered amine compound or hindered phenol compound, with further preference given to hindered amine compound or combination of hindered amine compound and another medium from the view point of improvement in the color fastness to light of the organic photochromic compound.

Examples of the hindered phenol compound described above include 2,6-di-t-butylphenol, 2,4,6-t-butylphenol, 2,6-di-t-butyl-p-cresol, 4-hydroxymethyl-2,6-di-t-butylphenol, 2,5-di-t-butyl hydroquinone, 2,2'-methylene-bis(4-ethyl-6-t-butylphenol) and 4,4'-butylidene-bis(3-methyl-6-t-butylphenol).

Examples of the hindered amine compound described above include bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, polycondensation product of dimethyl succinate and 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine, poly[(6-(1,1,3,3-tetramethylbutyl)-amino-1,3,5-triazine-2,4-diy1)[2,2,6,6-tetramethyl-4-piperidyl]limino] hexamethylene(2,2,6,6-tetramethyl-4-piperidyl)limino], 2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-n-butylmalonic acid bis(1,2,2,6,6-pentamethyl-4-piperidyl), 1-[2-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionyloxy]-2,2,6,6-tetramethylpiperidine, 8-benzyl-7,9,9-tetramethyl-3-octyl-1,3,8-triazaaspiro[4,5]-undecane-2,4-dione, tetrakis(2,2,6,6-tetramethyl-4-piperidine)butanecarbonate and mark LA57, mark LA62 and mark LA67 (trade names, product of Adeka Argust Co.).

Examples of the high boiling solvent described above include high-boiling or slow-evaporating kinds of alcohols, ketones, esters, ethers, aromatic (halogenated) hydrocarbons, aliphatic (halogenated) hydrocarbons, ethylene glycol ethers, formamides and sulfoxy compounds.

Examples of the plasticizer described above include all plasticizers such as phthalate-based plasticizers, adipate-based plasticizers, phosphate-based plasticizers, polyester-based plasticizers and polyether-based plasticizers.

Examples of the above synthetic resin include similar synthetic resins as in fine particles of thermochromic matrix described above.

Examples of dyeing process

Dyeing of a cellulose fiber textile product by the dyeing method of the present invention can be achieved for example as follows:

The textile product described above is first scoured to remove sizing and impurities. Scouring is of course unnecessary when the textile product is clean.

Next, to an appropriate dyeing bath, water in an amount 5 to 50 times the amount of the textile product (bath ratio = 1:5 to 1:50), preferably 10 to 30 times (bath ratio = 1:10 to 1:30), is added, and a cationic compound is added thereto in a ratio of about 0.1 to 20% by weight, preferably about 0.3 to 5% by weight, to the pretreatment textile product. An acid such as acetic, tartaric, oxalic or malic acid may be added to adjust the pH to the acidic side, or a wetting agent such as urea, glycerol, ethylene glycol, polyethylene...
glycol or diethylene glycol may be added to improve the permeability of the cationic compound into the textile product.

Next, the textile product described above is immersed in the aqueous solution thus obtained, and the temperature is maintained at normal temperature to about 80 °C for about 5 to 30 minutes, whereby the cellulose fiber of the textile product is efficiently cationized.

Subsequently, this textile product is thoroughly rinsed to wash down the excess portion of the cationic compound and other additives and then dehydrated.

Next, to the bath containing the treated textile product, water is added in a ratio of about 1:5 to 1:50, preferably 1:10 to 1:30, relative to the pretreatment textile product, and the reversibly color changeable fine particles as described above are added and dispersed in a ratio of about 0.1 to 50% by weight, preferably 1 to 25% by weight, relative to the pretreatment textile product. It is possible to add the fine particles in the form of aqueous dispersion containing them.

The dispersion thus obtained is treated at normal temperature to about 90 °C for 5 to 30 minutes, whereby the reversibly color changeable fine particles are completely exhausted into the cationized textile product described above. This treatment temperature is preferably about 60 to 90 °C when using the fine particles described above at a high concentration of 10 to 50% by weight.

This treatment results in the binding of the reversibly color changeable fine particles described above to the textile product described above by chemical ion bond and physical adsorption. This product is then dehydrated and dried and heated at preferably about 80 to 180 °C for about 0.5 to 10 minutes, whereby the fine particles described above are firmly fixed to the textile product.

The textile product thus obtained has been dyed with the reversibly color changeable fine particles to a high density and in addition, it maintains a good texture and soft handling touch, and it is excellent in color fastness to rubbing and color fastness to washing.

Example of preferable dyeing process 1

A preferred mode of the dyeing method of the present invention comprises:
a process of treating a cellulose fiber textile product with cationic compound;
another process of treating the thus-treated textile product by immersing it in a dispersion containing reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound; and
still another process of further treating the textile product by adding binder to the dispersion in an amount insufficient to spoil the appearance and touch of the dyed product.

The binder solid content can be 0.1 to 10% by weight of the textile product in general. The binder solid content is more preferably 0.3 to 5% by weight.

Examples of the usable binder include acrylic resin, methacrylic acid resin, vinyl acetate resin, polyurethane resin, polyester resin, styrene-butadiene latex and polyolefin resin; polyacrylic acid, methacrylic acid and their derivatives and copolymers of these substances with other vinyl polymers. For the present invention, acrylic ester resin and polyurethane resin are especially preferable.

Dyeing a textile product by this method can be achieved, for example, as follows: The cellulose fiber textile product is treated with a cationic compound and immersed in dispersion containing reversibly color changeable fine particles. The fine particles are thereby exhausted into the textile product. To the dispersion, a binder is added in a ratio of 0.1 to 10% by weight of binder solid content relative to the textile product, followed by treatment at normal temperature to about 90 °C for 1 to 30 minutes and dehydration and drying.

The textile product thus obtained shows further improvements in the color fastness to rubbing and color fastness to washing.

Example of preferable dyeing process 2

Another preferred mode of the dyeing method of the present invention comprises:
a process of treating a cellulose fiber textile product with cationic compound;
another process of treating the thus-treated textile product by immersing it in a dispersion containing reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound; and
still another process of further treating the textile product by immersing it in water containing binder in an amount insufficient to spoil the appearance and touch of the dyed product.

This binder can be the same as above. The binder solid content can be 0.1 to 10% by weight to the
textile product in general. The binder solid content is more preferably 0.3 to 5% by weight.

Dyeing a textile product by this method can be achieved, for example, as follows: The cellulose fiber textile product is treated with a cationic compound and immersed in dispersion containing reversibly color changeable fine particles. The fine particles are thereby exhausted into the textile product, followed by dehydration. To the bath, water is added in a bath ratio of 1:5 to 1:50, preferably 1:10 to 1:30. A binder is added in a ratio of 0.1 to 10% by weight of binder solid content relative to the textile product, followed by treatment at normal temperature to about 90 °C for 5 to 30 minutes and dehydration and drying.

The textile product thus obtained shows further improvements in the color fastness to rubbing and color fastness to washing similarly in the case described above.

Example of preferable dyeing process 3

A still another preferred mode of the dyeing method of the present invention comprises:

- a process of treating a cellulose fiber textile product with cationic compound; and
- another process of treating the thus-treated textile product by immersing it in a dispersion containing
  - a) reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound and
  - b) binder in an amount insufficient to spoil the appearance and touch of the dyed product.

This binder can be the same as above. The binder solid content can be 0.1 to 10% by weight to the textile product in general. The binder solid content is more preferably 0.3 to 5% by weight.

Dyeing a textile product by this method can be achieved, for example, as follows: The cellulose fiber textile product is treated with a cationic compound and immersed in dispersion containing reversibly color changeable fine particles and a binder in a ratio of 0.1 to 10% by weight of binder solid content relative to the textile product and treated at normal temperature to about 90 °C for 5 to 30 minutes, followed by dehydration and drying.

The textile product thus obtained shows further improvements in the color fastness to rubbing and color fastness to washing similarly in the case described above.

Example of preferable dyeing process 4

A still another preferred mode of the dyeing method of the present invention comprises:

- a first process of treating a cellulose fiber textile product with cationic compound and binder in an amount insufficient to spoil the appearance and touch of the dyed product; and
- a second process of treating the thus-treated textile product by immersing it in a dispersion containing reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound.

This binder can be the same as above. The binder solid content can be 0.1 to 10% by weight of the textile product in general. The binder solid content is more preferably 0.3 to 5% by weight.

In the first process, neutralization of cationic compound by adding soda ash or caustic soda is carried out at need.

The first process can be replaced by the process of treating a cellulose fiber textile product with cationic binder in an amount insufficient to spoil the appearance and touch of the dyed product.


In the above described preferable dyeing processes 1 to 4, the binder is exhausted into the textile product in an amount approximately equal to the content of the dispersion, i.e. in a ratio of about 0.1 to 10% by weight of binder solid content relative to the textile product, the binder is strongly fixed to the textile product by dehydration and drying. As a result, further improvements in the color fastness to rubbing and color fastness to washing are obtained. The binder solid content is less than 0.1% by weight relative to the textile product, the obtained effect is likely to be insufficient. If the binder content exceeds 10% by weight, the appearance and touch of the textile are often spoiled.

By the use of two or more kinds of thermochromic fine particles whose color changing temperatures are different, it is possible that the dyed products of the present invention change color in two or more stages,
like "yellow ← → orange ← → black".

By the use of specific esters as solvent of the three-component mixture in thermochromic fine particles, it is possible that the dyed product shows obvious hysteresis in changing color. For example, the temperature of development of the color with a drop in temperature can be lower by some centigrade degrees than the temperature of disappearance of the color with a rise in temperature. Accordingly, it is possible for a uniformly dyed textile product of the present invention to show different colors in parts at equal temperature.

Dyeing a textile product by the present dyeing method with mixture of thermochromic fine particles and photochromic fine particles, the dyed product changes color in plural stages reversibly by changing the temperature or in the presence or absence of light irradiation.

Furthermore, in the dyeing method of the present invention described above, the dispersion containing reversibly color changing fine particles may further contain daylight fluorescent pigment and/or other inorganic or organic pigments, which may be exhausted into the textile product simultaneously with the reversibly color changing fine particles.

This makes it possible to cause reversible color changes, which are developed by color mixture of the pigment and the fine particles, by changing temperature or in the presence or absence of light irradiation.

Any addition amount of the pigment described above can be selected as long as the total amount of the reversibly color changing fine particles and pigment does not exceed 50% by weight of the textile product. It is preferable to use the pigment in a ratio of 0.5 to 10% by weight in the case of daylight fluorescent pigments, or 0.1 to 2% by weight in the case of other inorganic pigments or organic pigments.

Examples of daylight pigments include those prepared by coloring a formaldehyde condensation product of cyclic aminotriazine compound and aromatic monosulfamide compound as the base resin with a fluorescent cation dye or dispersion dye. Other pigments include inorganic pigments such as iron oxide, chromium yellow, ultramarine blue, titanium dioxide and carbon black, and organic pigments such as azo pigments, anthraquinone pigments, lake pigments, dioxazine pigments and phthalocyanine pigments.

These pigments can be used in the form of a dispersion of fine grains having a diameter of 0.05 to 10 μm prepared by wet milling in water containing the anionic surfactant described above and the nonionic surfactant and wetting agent described above added as needed.

Also, in the presence of an anionic surfactant and if necessary nonionic surfactant, a daylight fluorescent pigment obtained by coloring an aqueous emulsion polymer or suspension polymer of acrylonitrile and another polymerizable unsaturated vinyl compound with a fluorescent cationic dye or dispersion dye upon or after polymerization can be used as such, since it is about 0.05 to 10 μm in grain diameter.

Furthermore, it is also possible to color the textile product in advance and subject it to any one mode of the dyeing method of the present invention described above.

Accordingly, when any one of the dyeing methods described above is carried out after dyeing the textile product with a direct dye or acid dye or after basically dyeing the textile product with a pigment such as an organic pigment, inorganic pigment or daylight fluorescent pigment by resin padding, it is possible to cause reversible color changes, which are developed by color mixture of the pigment and the fine particles, by changing temperature or in the presence or absence of light irradiation.

PREPARATION EXAMPLES OF REVERSIBLY COLOR CHANGING FINE PARTICLES

Some preparation examples of reversibly color changing fine particles are given below. In the following description, "part(s) by weight" are simply referred to as "part(s)".

PREPARATION EXAMPLE 1

-- preparation of thermochromic microcapsule containing three-component mixture --

NC-R-1(pink) (trade name, acid developing substance, product of Hodogaya Chemical Industry Co.) 1 part
Bisphenol A 2 parts
Bisbenzotriazole-5-methane 2 parts
Lauryl palmitate 10 parts
Cetyl alcohol 10 parts
Tinuvin 326 (trade name, ultraviolet absorbent, product of Chiba-Geigy AG) 2 parts
Epikote 828 (trade name, epoxy resin, product of Yuka Shell Epoxy Co.) 6 parts

A hot uniform molten mixture of the formulation described above was obtained by heating it. The
molten mixture was added to 200 parts of a 5% aqueous solution of gelatin at 60 °C and dispersed in the form of oil droplets of 5 μm in diameter with stirring.

Then, 4 parts of an epoxy resin hardener (EPICURE U (tradename), product of Yuka Shell Epoxy Co.) was added, and stirring was continued and the temperature was increased to 90 °C, followed by reaction for 2 hours.

The solution was thereafter cooled, and the resulting microcapsules were washed with water and filtered to remove 90% by weight of the gelatin contained therein to yield 100 parts of a dispersion containing about 35 parts of thermochromic microcapsules and about 1 part of gelatin.

**PREPARATION EXAMPLE 2**

-- preparation of photochromic microcapsule --

100 parts of a dispersion containing 35% by weight of photochromic microcapsules was obtained in the same manner as in Preparation Example 1 except that 1 part of 1,3,3-trimethylspiro[indoline-2,3'-[3H]-naphtho(2,1-b)(1,4)oxazine] (organic photochromic compound) and 26 parts of bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate were used in place of the NC-R-1, bisphenol A, bisbenzotriazole-5-methane, lauryl palmitate, cetyl alcohol and Tinuvin 326 used in Preparation Example 1.

**PREPARATION EXAMPLE 3**

-- preparation of thermochromic microcapsule containing three-component mixture --

150 parts of water, 7.5 parts of urea and 20 parts of 37% formalin were mixed. This mixture was adjusted to a pH of 8 with 10% sodium carbonate and stirred at 70 °C for 1 hour to yield an aqueous solution containing an initial condensation product of urea and formaldehyde.

Then, to this solution, the molten mixture of the formulation described below was added dropwise with stirring, and stirring was continued at a stirring rate adjusted so that the grain diameter of this mixture became about 5 μm.

Y-1 (leuco dye (yellow), product of Yamamoto Kasei Co.) 1 part
Bisphenol A 4 parts
Myristyl alcohol 10 parts
Lauryl palmitate 10 parts
Tinuvin 328 2 parts

Citric acid was added dropwise to adjust the liquid to a pH of 5, and the liquid was stirred at 70 °C for 2 hours. Citric acid was further added dropwise to adjust the liquid to a pH of 3, and the solution was stirred at 80 °C for 2 hours, followed by washing with water, filtration and drying to yield about 40 parts of microcapsules.

Next, the microcapsules described above were added to 100 parts of 2% carboxymethyl cellulose, and this mixture was stirred to yield a uniform dispersion.

To this dispersion, 100 parts of 2% polyvinyl alcohol were added. After the temperature was increased to 40 °C, 100 parts of 25% sodium chloride were gradually added with stirring, and the dispersion was subsequently cooled to 10 °C, and 50% glutaraldehyde was added with additional stirring, followed by stirring for 15 hours.

After the temperature was increased to 40 °C, the liquid was stirred at 40 °C for 3 hours, followed by washing with water, filtration and drying to yield about 42 parts of microcapsules whose outer layer were coated with carboxymethyl cellulose.

**PREPARATION EXAMPLE 4**

-- preparation of photochromic microcapsule --

2,2-diphenyl-3H-naphtho-(2,1-b)pyran 1 part
Tinuvin 622LD (trade name, hindered amine compound, product of Chiba-Geigy AG) 2 parts
Polystyrene resin 24 parts
Toluene 56 parts
Polymethylene-n-phenyl isocyanate [MILLIONATE MR (trade name, product of Nippon Polyurethane Industry Co., Ltd.)] 10 parts
This formulation was stirred in a sand grinder to yield a uniform liquid mixture.

Separately, 500 parts of an aqueous solution containing 2 parts of colloidal calcium phosphate was prepared, to which the uniform liquid mixture described above was added dropwise with stirring, followed by stirring for about 1 hour at an adjusted stirring rate to yield a suspension of uniform dispersion of about 5 \( \mu \text{m} \) in average grain size with the almost all portion of the toluene evaporated.

Stirring was continued and 2 parts of xylylenediamine was added dropwise and the suspension was stirred for 3 hours, after which it was filtered, washed with water, and dried to yield about 38 parts of photochromic microcapsules.

PREPARATION EXAMPLE 5

-- preparation of photochromic microcapsule --

Photochromic microcapsules were obtained in the same manner as in Preparation Example 4 except that 1 part of 6'-piperidino-1,3,3-trimethylspiro[indoline-2,3'-[3H]naphtho(2,1-b)(1,4)oxazine] and 26 parts of SANOL LS-770 were used in place of 1 part of 2,2-diphenyl-3H-naphtho-(2,1-b)pyran, 2 parts of Mark LA-67, 24 parts of polystyrene resin and 56 parts of toluene used in Preparation Example 4.

PREPARATION EXAMPLE 6

-- preparation of fine particle of photochromic matrix --

8'-piperidino-1,3,3-trimethylspiro[indoline-2,3'-[3H]naphtho(2,1-b)(1,4)oxazine] (organic photochromic compound) 1 part 20
Mark LA-67 2 parts 25
DIANOL SE-5377 (trade name, 40% by weight of polymethyl methacrylate resin, 60% by weight of xylene, product of Mitsubishi Resin Co., Ltd.) 60 parts 30
Xylene 20 parts

The molten mixture of the formulation described above was added dropwise to a 3% aqueous solution of styrene/maleic anhydride copolymer with stirring. And the mixture was stirred at 80 to 90 °C for about 2 hours at an adjusted stirring rate to yield a suspension of uniform dispersed phase having about 5 \( \mu \text{m} \) average grain size with the almost all portion of the xylene evaporated. The suspension was washed with water, filtrated and dried to yield 38.5 parts of fine particles of photochromic matrix involve about 0.5 part of styrene/maleic anhydride copolymer.

PREPARATION EXAMPLE 7

-- preparation of fine particle of thermochromic matrix

Aqueous solution containing DEMOL N (trade name, anionic surfactant, product of Kao Co.) was heated to 90 °C. To this solution, the molten uniform mixture of the formulation described below was added dropwise with stirring the solution.

NC-R-1 0.4 part 20
Bisphenol A 1.6 part
Behenyl alcohol 3 parts 25
Sanwax 151P (trade name, low molecular weight polypropylene, product of Sanyo Kasei Kogyo Co.) 5 parts 30
STAFLENE E-715 (trade name, polyethylene resin, product of Nippon Sekiyu Kagaku Kogyo Co.) 50 parts
Xylene 20 parts

And the mixture was stirred at 90 °C for about 2 hours to yield a suspension containing fine particles of thermochromic matrix having about 10 \( \mu \text{m} \) average grain size with the almost all portion of the xylene evaporated.

The suspension was concentrated by water evaporation to yield 150 parts of suspension containing about 60 parts of the fine particles of thermochromic matrix with the xylene perfectly evaporated.

PREPARATION EXAMPLE 8

-- preparation of thermochromic microcapsule containing three-component mixture having character of hysteresis --

12
A dispersion involving thermochromic microcapsules containing three-component mixture having character of hysteresis was obtained in the same manner as in Preparation Example 1 except that 15 parts of stearyl benzoate and 5 parts of lauryl myristate were used in place of 10 parts of lauryl palmitate and 10 parts of cetyl alcohol used in Preparation Example 1.

EXAMPLES

Some examples are given below. But the present invention is not limited by these examples.

EXAMPLE 1

A cotton T-shirt (grey sheeting, 120 parts) was scoured to remove the sizing and impurities.

Next, 2400 parts of water (bath ratio = 1:20), 2 parts of SANFIX PAC-7 (trade name, aqueous solution of quaternary ammonium salt type cationic polymer compound, product of Sanyo Kasei Kogyo Co.) and 1075 parts of ethylene glycol were added to a 5-l vat.

The scoured T-shirt described above was immersed in this aqueous solution and gradually heated to 70 °C, at which temperature it was treated for 15 minutes.

Subsequently, the T-shirt was thoroughly rinsed with water to remove the excessive portion of the cationic compound and other additives, followed by dehydration.

Next, 2400 parts of water and 50 parts of a dispersion containing the thermochromic microcapsules obtained in Preparation Example 1 were added to this vat, and this liquid was gradually heated to 80 °C, at which temperature it was treated for 15 minutes.

This dispersion was pink before treatment, but it became a transparent colorless liquid after treatment (observation was made at 25 °C). This finding demonstrates that the thermochromic microcapsules were completely exhausted into the cotton T-shirt.

Subsequently, this T-shirt was thoroughly rinsed and dehydrated, after which it was allowed to dry and then subjected to heat treatment at 140 °C in a tumbler drier for 1 minutes.

When the T-shirt thus obtained was worn, its entire surface changed in its color among white, distinct pink, pinkish white, etc. according to heat transmission from body temperature and minute changes in atmospheric temperature.

The appearance, handling touch, color fastness to rubbing and color fastness to washing of the T-shirt were all good.

EXAMPLE 2

A cotton T-shirt was treated in the same manner as in Example 1 except that the suspension containing the fine particles of thermochromic matrix of Preparation Example 7 was used in place of the dispersion containing thermochromic microcapsules obtained in Preparation Example 1. The treated T-shirt showed same color changes as in Example 1, and the quality of the T-shirt was as good as in Example 1.

EXAMPLE 3

A cotton T-shirt was treated in the same manner as in Example 1 except that the dispersion containing the photochromic microcapsules of Preparation Example 2 was used in place of the dispersion containing thermochromic microcapsules obtained in Preparation Example 1.

This treated T-shirt was found to be white under indoor conditions free of direct sun light, while it became dark blue at windows and outdoors under direct sun light. This change could be reversibly repeated in cycles, and the quality of the T-shirt was as good as in Example 1.

EXAMPLE 4

A cotton T-shirt was treated in the same manner as in Example 1 except that the fine particles of photochromic matrix of Preparation Example 6 were used in place of the thermochromic microcapsules obtained in Preparation Example 1.

This treated T-shirt was found to be white under indoor conditions free of direct sun light, while it became deep purple at windows and outdoors under direct sun light. This change could be reversibly repeated in cycles, and the quality of the T-shirt was as good as in Example 1.
EXAMPLE 5

A cotton T-shirt was treated in the same manner as in Example 1 except that 20 parts of the dispersion containing the thermochromic microcapsules of Preparation Example 1 and 30 parts of the dispersion containing the photochromic microcapsules of Preparation Example 2 were used in place of 50 parts of the dispersion containing thermochromic microcapsules obtained in Preparation Example 1.

Color of this treated T-shirt changed among white, blue, pink and deep purple reversibly through various paths by changing temperature or in the presence or absence of light irradiation. The quality of the T-shirt was as good as in Example 1.

EXAMPLE 6

A cotton T-shirt was treated in the same manner as in Example 1 except that 10 parts of the dispersion containing the thermochromic microcapsules of Preparation Example 1 and 8 parts of the photochromic microcapsules of Preparation Example 3 were used in place of 50 parts of the dispersion containing thermochromic microcapsules obtained in Preparation Example 1.

This treated T-shirt was found to be white at temperatures over about 30 °C, while it became pink at about 25 °C, and it became deep orange at temperatures about below 20 °C, i.e. changed color in two stages. This change could be reversibly repeated in cycles, and the quality of the T-shirt was as good as in Example 1.

EXAMPLE 7

First, a cotton T-shirt scoured in the same manner as in Example 1 was immersed in an aqueous solution of a bath ratio of 1:20 prepared by adding a direct dye (trade name, KAYARUS YELLOW F8G, product of Nippon Kayaku Co., Ltd.) to water in a ratio of 0.1%, and treated at 90 °C for 3 minutes to yield a yellow dyed T-shirt.

The T-shirt was obtained in the same manner as in Example 1 except that the yellow dyed T-shirt was used in place of the scoured cotton T-shirt of Preparation Example 1 and the dispersion containing the thermochromic microcapsules of Preparation Example 8 was used in place of the dispersion containing thermochromic microcapsules obtained in Preparation Example 1.

This T-shirt was found to be deep orange which is developed by mixing pink of the thermochromic microcapsules and yellow of the ground color at temperatures about below 25 °C, while it changed its color to yellow at temperatures about over 30 °C as the color of the microcapsules disappeared.

The color of the T-shirt remained yellow at temperatures about over 20 °C; as the temperature decreased the color changed to deep orange again at temperatures about below 15 °C.

Accordingly, this T-shirt shows yellow and deep orange simultaneously at temperatures ranged 20 to 25 °C by partial difference of temperature hysteresis.

The quality of the T-shirt was as good as in Example 1.

EXAMPLE 8

A cotton T-shirt (smooth knit, 150 parts) was scoured to remove the sizing and impurities.

Next, an aqueous solution containing 3000 parts of water (bath ratio = 1:20), 1.5 parts of AMIGEN NF (tradename, aqueous solution containing quaternary ammonium salt type cationic polymer compound about 30% by weight, product of Dai-ichi Kogyo Seiyaku Co., Ltd.) and 10 parts of ethylene glycol were added to a 5-t vat. The T-shirt described above was immersed in this solution and gradually heated to 60 °C, at which temperature it was treated for 20 minutes.

Subsequently, this T-shirt was thoroughly rinsed with water and dehydrated. Next, 3000 parts of water and 22.5 parts of the photochromic microcapsules obtained in Preparation Example 4 were added to this vat and dispersed. This dispersion was gradually heated to 70 °C, at which temperature it was treated for 15 minutes to exhaust the photochromic microcapsule into this T-shirt.

Subsequently, this T-shirt was thoroughly rinsed with water and dehydrated, after which it was subjected to tumbler drying for 1 minute.

The obtained T-shirt was found to be totally white under indoor conditions free of direct sunlight, while it changed its color to deep yellow at windows and outdoors under direct sun light by developing color of the photochromic microcapsules. This change could be reversibly repeated in cycles, and the quality of the T-shirt was as good as in Examples 1 through 7.
EXAMPLE 9

Photochromic microcapsules were exhausted into a cotton T-shirt (150 parts, smooth knit), and the T-shirt was rinsed with water and dehydrated in the same manner as in Example 8.

Next, 3000 parts of water and 15 parts (solid content = about 4.5 parts) of MATSUMINSOL MR-10 (trade name, acrylic ester resin binder, product of Matsui Shikiso Chemical Co., Ltd.) were added to the vat containing the T-shirt and this mixture was gradually heated to 70 °C, at which temperature it was treated 15 minutes and then dehydrated and dried.

The obtained T-shirt showed the same color changes as in Example 8 and had almost equal appearance and touch to those of the T-shirt of the Example 8. Moreover, the color fastness to rubbing and color fastness to washing were better than those of the T-shirt of Example 8.

COMPARATIVE EXAMPLE 1

A T-shirt as used in Example 8 was scoured and then immersed in a padding solution comprising 1300 parts of water, 300 parts of the photochromic microcapsules of Preparation Example 4 and 400 parts of MATSUMINSOL MR-10 by the two-dip two-nip method and then dehydrated and allowed to dry.

However, large amounts of photochromic microcapsules and binder were used in the water, this T-shirt was found to be white under indoor conditions free of sufficient light. When irradiated with sufficient light, this T-shirt changed its color to pale yellow, but this change was too minute to notice without careful watching, and it seemed to have no commercial value. In addition, the color fastness to rubbing and color fastness to washing were poorer than those of the T-shirt of Example 8.

Results of comparison of this T-shirt with the T-shirts obtained in Examples 8 and 9 are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Coloring density</th>
<th>Touch and appearance</th>
<th>Color fastness to rubbing</th>
<th>Color fastness to washing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 8</td>
<td>100</td>
<td>Nearly the touch and appearance of cotton, with soft touch</td>
<td>Grade 3</td>
<td>Grade 3</td>
</tr>
<tr>
<td>Example 9</td>
<td>100</td>
<td>Almost the same as in Example 8</td>
<td>Grade 4</td>
<td>Grade 4</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>20</td>
<td>Hard</td>
<td>Grade 2 to 3</td>
<td>Grade 2 to 3</td>
</tr>
</tbody>
</table>

In Table 1, the color fastness to rubbing and color fastness to washing were evaluated on the basis of Japan Industrial Standard JIS L-0849 and L-0844 Method A-2, respectively.

EXAMPLE 10

A photochromic microcapsule was exhausted into a cotton T-shirt (150 parts, smooth knit) in the same manner as in Example 8 except that the photochromic microcapsules of Preparation example 5 were used in place of the photochromic microcapsules of Preparation example 4. Subsequently, 15 parts (solid content = about 4.5 parts) of MATSUMINSOL MR-10 was added to the bath and the T-shirt was treated at 60 °C for 15 minutes, after which it was dehydrated and dried.

This T-shirt was found to be totally white under indoor conditions free of direct sunlight, while it changed its color to deep purple at windows and outdoors under direct sun light.

This change could be reversibly repeated in cycles, and in addition the appearance, handling touch, color fastness to rubbing and color fastness to washing were as good as in Example 9.

EXAMPLE 11

A T-shirt was cationized in the same manner as in Example 8.

Subsequently, this T-shirt was thoroughly rinsed with water and then dehydrated. Then, 3000 parts of water, 17.5 parts of the photochromic microcapsules of Preparation example 4 and 7.5 parts of Glow Pink MI2G (trade name, water dispersion of pink daylight fluorescent pigment in the presence of anionic surfactant, product of Matsui Shikiso Chemical Co., Ltd.) were added to this vat and dispersed, followed by
the same procedure as in Example 8 to yield a T-shirt on the entire surface of which the photochromic microcapsule and the daylight fluorescent pigment were fixed.

This T-shirt was found to be totally pink under indoor conditions free of direct sun light, while it changed its color to deep orange at windows and outdoors under direct sunlight by mixing pink of the pigment and yellow of the photochromic microcapsules. This change could be reversibly repeated in cycles, and the quality of the T-shirt was as good as in Example 8.

EXAMPLE 12

First, a cotton trainer (300 parts) was scoured to remove the sizing and impurities.

Next, to a 10-l vat, 6000 parts of water, 2.7 parts of SANFIX 70 (trade name, dicyanamide type cationic polymer compound, product of Sanyo Kasei Co., Ltd.) and 15 parts of ethylene glycol were added, and the trainer described above was immersed in this liquid and treated at 60 °C for 15 minutes and then thoroughly rinsed and dehydrated.

Next, 6000 parts of water was added to this vat, and 15 parts of the thermochromic microcapsule of Preparation example 3 were added and dispersed.

This dispersion was gradually heated to 70 °C, at which temperature it was treated for 15 minutes, after which it was thoroughly rinsed and dehydrated. Then, 6000 parts of water was added and 30 parts (solid content = about 9 parts) of HYDRIN AP-20 (trade name, polyurethane resin emulsion, product of Dainippon Ink and Chemicals, Inc.) was added, and this solution was gradually heated to 70 °C, at which temperature it was treated for 15 minutes, after which it was dehydrated and allowed to dry.

This trainer was found to be yellow at temperatures below about 20 °C, but it became white at about 25 °C. This change could be reversibly repeated in cycles. In addition, the appearance, handling touch, color fastness to rubbing and color fastness to washing of the trainer were as good as in Example 9.

EXAMPLE 13

A cotton trainer (300 parts) was scoured and cationized in the same manner as in Example 12, after which it was thoroughly rinsed and dehydrated.

Next, 6000 parts of water were added to the vat containing this dehydrated cotton trainer, and 45 parts of the thermochromic microcapsules of Preparation example 3 and 30 parts of HYDRIN AP-20 were added and dispersed.

This dispersion was gradually heated to 80 °C, at which temperature the cotton trainer was treated for 15 minutes, after which it was dehydrated and allowed to dry thoroughly.

This trainer showed the same color changes as in Example 12, and its appearance, touch, color fastness to rubbing and color fastness to washing were as good as in Example 12.

EXAMPLE 14

First, a cotton trainer (300 parts) was scoured to remove the sizing and impurities.

Next, to a 10-l vat, 6000 parts of water, 30 parts (solid content = about 12 parts) of CGC-102 (trade name, acrylate resin emulsion, product of Sumitomo Chemical Co., Ltd.) and 15 parts of ethylene glycol were added, and the trainer described above was immersed in this liquid and treated at 70 °C for 15 minutes and then thoroughly rinsed and dehydrated.

Next, 6000 parts of water were added to this vat, and 45 parts of the thermochromic microcapsules of Preparation Example 3 and 6 parts of PG BLUE-MI-IB (tradename, aqueous dispersion containing blue organic pigment about 20% by weight, product of Matsui Shikiso Chemical Co., Ltd.) were added and dispersed.

This dispersion was gradually heated to 80 °C, at which temperature it was treated for 15 minutes, after which it was thoroughly rinsed, dehydrated and allowed to dry. And then, it was subjected to heat treatment at 130 °C for 3 minutes.

This trainer was found to be dark green at temperatures below about 20 °C by mixing blue of the organic pigment and yellow of the thermochromic microcapsules, but it became blue at temperatures about over 25 °C as the color of the microcapsules disappeared.

This change could be reversibly repeated in cycles. In addition, the appearance, handling touch, color fastness to rubbing and color fastness to washing of the trainer were as good as in Example 12.

EXAMPLE 15
A trainer as used in Example 12 was scoured. 6000 parts of water and 6 parts of KAYARUS Black G conc (trade name, direct dye, product of Nippon Kayaku Co., Ltd.) were added to a vat, and this trainer was immersed therein and heated to 90 °C, at which temperature it was treated for 5 minutes and then rinsed with water and dehydrated to dye this trainer black.

Next, the black trainer was treated in the same manner as in Example 12 except that the dispersion containing 40% by weight of the thermochromic microcapsules involving below described liquid crystals.

This trainer reversibly changed its color clearly among red, yellow, green, blue and purple at temperatures ranged about 18 to 30 °C. The quality of the trainer was as good as that of the trainer of Example 12.

The thermochromic microcapsule involving above described liquid crystals can be obtained by carrying out coacervation method using the liquid crystals consisting of cholesterol nonanate, cholesterol benzoate and cholesterol oleyl carbonate whose ratio is 1:1:1 by weight, gelatin and gum arabic.

EXAMPLE 16

Cotton jeans were scoured in a Smith drum dyeing machine.

Next, the jeans were squeezed and were immersed in an aqueous liquid (bath ratio = 1:15) containing 2% by weight of AMIGEN NF relative to the jeans and 10% by weight (solid content = about 4% by weight relative to the jeans) of CGC-102, it was treated for 2 minutes at 30 °C. Subsequently, 0.3% by weight of NaOH relative to the jeans was added to the liquid, after treated for 10 minutes at 30 °C, rinsed and dehydrated.

Next, the jeans were immersed in an aqueous liquid (bath ratio = 1:15) containing 10% by weight of thermochromic microcapsules of Preparation example 3 relative to the jeans and 4% by weight of PG BLUE-MI-IB relative to the jeans, treated for about 10 minutes at 75 °C, rinsed and allowed to dry. In addition, the jeans were subjected to heat treatment at 140 °C for 3 minutes.

The jeans were found to be striped white and dark green at temperatures below about 20 °C by mixing blue of the organic pigment and yellow of the thermochromic microcapsules, but became striped white and blue at temperatures about over 25 °C as the color of the microcapsules disappeared.

This change could be reversibly repeated in cycles. The appearance and handling touch were almost equally good to untreated jeans, color fastness to rubbing and color fastness to washing thereof were as good as in Example 12.

COMPARATIVE EXAMPLES 2 THROUGH 5

The same procedures as in Examples 1, 6, 8 and 10 were followed except that no cationic compound was used.

The respective products thus obtained were found to have no commercial value because their coloring density was as low as about 10% in comparison with the clothes of Examples.

By way of explanation it is added that the terms "hindered amine compound" and "hindered phenol compound", as used in this description, refer to compounds in which the amine or phenolic hydroxy groups are surrounded by bulky groups (for example, plural methyl groups).

Claims

1. Dyeing method comprising:
a process of treating a cellulose fiber textile product with cationic compound; and
another process of treating the thus-treated textile product by immersing it in a dispersion containing reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound.

2. Dyeing method comprising:
a process of treating a cellulose fiber textile product with cationic compound;
another process of treating the thus-treated textile product by immersing it in a dispersion containing reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound; and
still another process of further treating the textile product by adding binder to the dispersion in an amount insufficient to spoil the appearance and touch of the dyed product.
3. Dyeing method comprising:
   a process of treating a cellulose fiber textile product with cationic compound;
   another process of treating the thus-treated textile product by immersing it in a dispersion containing
   reversibly color changeable fine particles which involve thermochromic or photochromic material in high
polymer compound; and
still another process of further treating the textile product by immersing it in water containing binder in
an amount insufficient to spoil the appearance and touch of the dyed product.

4. Dyeing method comprising:
a process of treating a cellulose fiber textile product with cationic compound; and
another process of treating the thus-treated textile product by immersing it in a dispersion containing
   a) reversibly color changeable fine particles which involve thermochromic or photochromic material
   in high polymer compound and
   b) binder in an amount insufficient to spoil the appearance and touch of the dyed product.

5. Dyeing method comprising:
a process of treating a cellulose fiber textile product with cationic compound and binder in an amount
insufficient to spoil the appearance and touch of the dyed product; and
another process of treating the thus-treated textile product by immersing it in a dispersion containing
reversibly color changeable fine particles which involve thermochromic or photochromic material in high
polymer compound.

6. Dyeing method comprising:
a process of treating a cellulose fiber textile product with cationic binder in an amount insufficient to
spoil the appearance and touch of the dyed product; and
another process of treating the thus-treated textile product by immersing it in a dispersion containing
reversibly color changeable fine particles which involve thermochromic or photochromic material in high
polymer compound.

7. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein said textile product is colored in advance.

8. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein said particles consist of fine particles involving
thermochromic material in high polymer compound and fine particles involving photochromic material in high
polymer compound.

9. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein said particles contain dispersed thermochromic
material selected from the group consisting of
   a) three-component mixture of acid developing substance, acidic substance and solvent,
   b) two-component mixture of acid developing substance and acidic substance and
   c) cholesteric liquid crystals
in matrix of synthetic resin.

10. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein said particles contain thermochromic material
    selected from the group consisting of
    a) three-component mixture of acid developing substance, acidic substance and solvent,
    b) two-component mixture of acid developing substance and acidic substance and
    c) cholesteric liquid crystals
    in high polymer microcapsules.

11. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein said particles contain dispersed organic photochromic
    substance in matrix of synthetic resin.

12. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein said particles contain dispersed organic photochromic
    substance in matrix of synthetic resin encapsulated in high polymer microcapsules.

13. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein said particles contain dissolved or dispersed organic
    photochromic substance in medium encapsulated in high polymer microcapsules.
14. Dyeing method of claim 1, 2, 3, 4, 5 or 6 wherein the diameters of said particles are not exceeding 50 μm.

15. Dyeing method of claim 10, 12 or 13 wherein the coat former for the high polymer microcapsule is one or more kinds of high polymer compound selected from the group consisting of polyurea, polyamide, polyester, polyurethane, epoxy resin, urea resin, melamine resin, gelatin, ethyl cellulose, ethylene/maleic anhydride copolymer, butylene/maleic anhydride copolymer, vinyl ether/maleic anhydride copolymer, anion-modified polyvinyl alcohol, gum arabic and carboxymethyl cellulose.

16. A dyed product, said product being cellulose fiber textile product pretreated with cationic compound and dyed with reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound.

17. A dyed product, said product being cellulose fiber textile product pretreated with cationic compound, dyed with reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound and treated with binder in an amount insufficient to spoil the appearance and touch of the dyed product.

18. A dyed product, said product being cellulose fiber textile product pretreated with cationic binder in an amount insufficient to spoil the appearance and touch of the dyed product and dyed with reversibly color changeable fine particles which involve thermochromic or photochromic material in high polymer compound.

19. The dyed product of claim 16, 17 or 18 wherein said textile product is colored in advance.

20. The dyed product of claim 16, 17 or 18 wherein said particles consist of fine particles involving thermochromic material in high polymer compound and fine particles involving photochromic material in high polymer compound.

21. The dyed product of claim 16, 17 or 18 wherein said particles contain dispersed thermochromic material selected from the group consisting of
   a) three-component mixture of acid developing substance, acidic substance and solvent,
   b) two-component mixture of acid developing substance and acidic substance and
   c) cholesteric liquid crystals in matrix of synthetic resin.

22. The dyed product of claim 16, 17 or 18 wherein said particles contain thermochromic material selected from the group consisting of
   a) three-component mixture of acid developing substance, acidic substance and solvent,
   b) two-component mixture of acid developing substance and acidic substance and
   c) cholesteric liquid crystals in high polymer microcapsules.

23. The dyed product of claim 16, 17 or 18 wherein said particles contain dispersed organic photochromic substance in matrix of synthetic resin.

24. The dyed product of claim 16, 17 or 18 wherein said particles contain dispersed organic photochromic substance in matrix of synthetic resin encapsulated in high polymer microcapsules.

25. The dyed product of claim 16, 17 or 18 wherein said particles contain dissolved or dispersed organic photochromic substance in medium encapsulated in high polymer microcapsules.

26. The dyed product of claim 16, 17 or 18 wherein the diameters of said particles are not exceeding 50 μm.

27. The dyed product of claim 22, 24 or 25 wherein the coat former for the high polymer microcapsule is
one or more kinds of high polymer compound selected from the group consisting of polyurea, polyamide, polyester, polyurethane, epoxy resin, urea resin, melamine resin, gelatin, ethyl cellulose, ethylene/maleic anhydride copolymer, butylene/maleic anhydride copolymer, vinyl ether/maleic anhydride copolymer, anion-modified polyvinyl alcohol, gum arabic and carboxymethyl cellulose.
## EUROPEAN SEARCH REPORT

**Application Number**: EP 91 11 4585

### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cl.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>GB-A-2 170 228 (PILOT INK CO LTD) * page 1, line 1 - page 5, line 39 **</td>
<td>1-6</td>
<td>D 06 P 1/00</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>7-27</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>7-27</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>CH-A-591 553 (VISIOTERM APPLICATIONS SA) * the whole document **</td>
<td>1-27</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>TEXTILE HORIZONS, vol. 8, no. 12, December 1980, MANCHESTER GB pages 45 - 47; STAN DAVIES: &quot;Japanese high technology yarns and fibres for fashion.&quot; * page 47, left column **</td>
<td>1-8</td>
<td></td>
</tr>
</tbody>
</table>

The present search report has been drawn up for all claims

<table>
<thead>
<tr>
<th>Place of search</th>
<th>Date of completion of search</th>
<th>Examiner</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Hague</td>
<td>16 January 92</td>
<td>DELZANT J-F.</td>
</tr>
</tbody>
</table>

### CATEGORY OF CITED DOCUMENTS

- **E**: earlier patent document, but published on, or after the filing date
- **D**: document cited in the application
- **L**: document cited for other reasons
- **&**: member of the same patent family, corresponding document
- **X**: particularly relevant if taken alone
- **Y**: particularly relevant if combined with another document of the same category
- **A**: technological background
- **O**: non-written disclosure
- **P**: intermediate document
- **T**: theory or principle underlying the invention