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EUROPEAN PATENT APPLICATION

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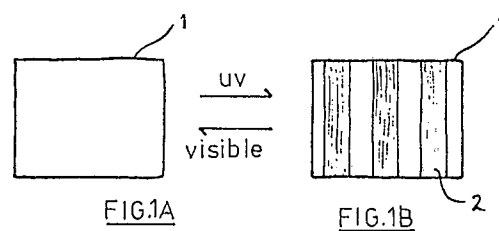
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⑤④ **Security device.**

⑤⑦ One or more threads of a photochromic yarn are used as a security device in woven material, for example a label (1). The threads are substantially colourless when irradiated with visible light but are reversibly converted to a coloured state (2) when irradiated with ultraviolet light.



Description

SECURITY DEVICE

This invention relates to a security device for use in marking articles such as goods, packages or identification cards to prove their authenticity.

The device is based on the use of photochromic compounds. A photochromic compound is a compound that undergoes a colour change when irradiated with light of a certain wavelength, which colour change is usually reversible. In general the compounds become coloured when irradiated with UV light and convert to a pale or colourless form in visible light.

It is known to use photochromic compounds by coating them onto or incorporating them into a support such as a film or plate. For example, GB-A-1,600,615 describes coating a film with a photochromic compound and using the coated film as a means for holographic data storage.

It has also been suggested to make photochromic fibre by dyeing fibre with a photochromic dye, or by incorporating photochromic compound into fibre. FR-A-1,588,282 describes a process for producing polyvinylidene chloride, polyester, polyacrylonitrile, polypropylene or polyamide fibre containing an indolino-spiropyran photochromic compound. The photochromic compound is incorporated into the spinning dope prior to spinning the fibre. Alternatively, the photochromic compound can be fixed to a fibre by soaking the fibre with a solution of the photochromic compound

JP-A-60-21975 describes a method for producing a photochromic fibre in which a spiropyran compound is mixed with a monomer, fibre is impregnated with the monomer and the monomer is polymerised within the fibre. It is stated that the fibre can be used for clothes, dresses, parasols and bags for special fashion effects.

JP-A-61-179399 describes the preparation of a photochromic fibre by causing photochromic transition metal acids to adhere to or be impregnated into various fibres, and reacting the resulting product with a water-soluble condensation resin or polymerisation resin. The fibres can be used as a raw material for the production of security paper or confidential documents.

The present invention is a novel application of photochromic compound for security purposes and accordingly provides a security device comprising woven material containing one or more threads of photochromic yarn, the yarn being substantially colourless when irradiated with visible light and reversibly converting to a coloured state when irradiated with UV light.

One suitable form of the device according to the invention is a label. The label can be attached, by way of sewing, adhering or the like, to an authentic article such as a garment, bag, towel, linen, blanket, carpet, fabric or other textile piece good, or a non-textile article, by the manufacturer. The photochromic yarn incorporated in the label is invisible under normal light conditions and so the label appears as an ordinary identification label. However, when the label is irradiated with UV light the photochromic yarn

becomes coloured and is visible to the naked eye. Any article not carrying a label with a colourable thread can be readily identified as counterfeit. After irradiation with UV light, the photochromic yarn will gradually revert to colourless under normal light conditions, or it can be rapidly converted back by irradiating the label with strong white light. The label then appears to be an ordinary identification label once more. UV light sources are widely available, portable and easy to use, the irradiation not normally taking longer than a few seconds. In addition the UV light does not damage the article to which the label is attached. Thus the device according to the invention provides a convenient, harmless and relatively inexpensive method of protecting authentic articles against counterfeiting.

In an alternative embodiment of the invention and where the authentic article to be protected is a woven article, such as a roll of fabric or other textile piece good, the photochromic yarn can be incorporated directly within the article by, for example, weaving a thread into its edge.

The photochromic yarn is preferably incorporated into the woven material of the security device by weaving. It may be incorporated as either a weft or warp yarn, but is preferably a weft yarn. The resulting material may contain any number of photochromic threads in any suitable pattern, depending upon the desired arrangement and complexity. Surprisingly it has been found that, for white or pale materials, one single thread of photochromic yarn is sufficient for yarn to be seen when the material is irradiated with UV light.

The photochromic yarn comprises fibre containing or treated with a photochromic compound or mixture of photochromic compounds. Two classes of generally suitable photochromic compounds are the spiropyran and spiro-oxazines, although their properties must be checked to ensure they are colourless or near-colourless under normal light conditions. Examples of spiro-pyrans and spiro-oxazines that can be used include 1',3',3'-trimethylindolino-6-nitrobenzospiropyran, 6,8-dichloro-1',3',3'-trimethyl-indolinobenzospiropyran and spiroindolinonaphthoxazine.

Other classes of suitable photochromic compounds are the fulgides and fulgimides. Examples of such compounds are described in GB-A-1,442,628, 1,464,603 and 2,170,202 and in our co-pending UK Patent Application 8830336, the disclosures of which are incorporated herein by reference.

The photochromic compound is preferably incorporated into the fibre prior to spinning, conveniently by dissolving or dispersing the photochromic compound into the spinning dope or melt. Any polymeric material can be used that is capable of containing a photochromic compound and being spun into a fibre without adversely affecting the photochromic compound, and that is transparent to light having the wavelength required to convert the photochromic compound from colourless to coloured or vice

versa. Examples of polymeric materials that can be spun into fibre from a spinning dope into which a photochromic compound is incorporated include cellulose acetate, acrylics, for example polyacrylonitrile or polymethylmethacrylate, polyurethanes, polycarbonates, vinyl polymers, for example polyvinylalcohol, polyvinylacetate or polyvinylchloride, and regenerated cellulose. Cellulose acetate, especially secondary cellulose acetate, is preferred. The photochromic compound is preferably dissolved in the spinning dope, so that it is more uniformly dispersed in the fibre formed. The photochromic fulgides, spiropyran and spiro-oxazines for instance are soluble in a wide range of organic solvents, for example ketones such as acetone or methylethyl ketone, esters such as ethyl acetate, aromatic hydrocarbons such as toluene, chlorinated hydrocarbons such as chloroform or methylene chloride, or ethers. They are not soluble in aliphatic hydrocarbons, are reactive to some extent with lower alcohols such as methanol and ethanol and are only sparingly soluble in water. The photochromic fulgides, spiropyran and spiro-oxazines, for example, can readily be incorporated in an acetone-based cellulose acetate dope. The photochromic compound may be mixed directly into the spinning dope, but it is preferred first to form a solution of the photochromic compound by dissolving the compound in a little of the spinning dope solvent and then mixing this into the dope. Alternatively the photochromic compound, in particulate form, may be dispersed into the spinning dope, this being necessary, for example, when the photochromic compound is insoluble in the spinning dope, as is the case when the spinning solvent is water.

Examples of polymer melts into which the photochromic compound can be dispersed prior to spinning include polyolefins for example polyethylene, polypropylene or copolymers thereof, polyesters for example polyethylene terephthalate, polycarbonates and polyamides.

Any conventional technique may be employed for spinning the fibre such as wet, dry, air-gap or melt spinning, although where melt spinning is carried out it is important that the temperature does not exceed that which would thermally degrade the photochromic compound.

The concentration of the photochromic compound in the resulting fibre is preferably 0.1 to 20% by weight based on the total weight of the fibre, more preferably 0.2 to 2%. Correspondingly the proportion of photochromic compound in the spinning dope is generally 0.01 to 10% by weight based on the total weight of the dope, more preferably 0.04 to 1%.

In an alternative embodiment, the photochromic fibre may have a core-sheath structure, the photochromic compound being incorporated in the sheath component. The polymeric material of the sheath component may be the same or different from the polymeric material of the core component.

The woven material that comprises the security device may be woven from any suitable textile yarn, for example cellulose acetate, viscose, solvent-spun cellulose, cotton, wool, silk, nylon, polyester or

acrylic yarn or a mixture thereof. Cellulose acetate or polyester is generally preferred.

The invention will now be illustrated by the following Examples and with reference to the accompanying drawings in which:

Figures 1A and 1B show a label before and after irradiation with UV light; and

Figures 2A and 2B show an alternative label before and after irradiation with UV light.

Irradiation with UV light was carried out using a 125W mercury arc lamp (Phillips HPR 125W) transmitted through a 3mm thick, 300-400nm band pass filter (Schott glass UG1). Irradiation with white light was carried out using a 375W photoflood lamp (Phillips PF215) transmitted through a 3mm thick, 420nm cut-off filter (Schott glass GG420).

Example 1

A solution of photochromic compound was first prepared by dissolving 5g of the fulgide alpha-2,5-dimethyl-3-furylethylidene (isopropylidene) succinic anhydride in 50ml acetone. The mixture was stirred for 2 hours to ensure complete dissolution.

The solution was then added to 2kg of acetone-based cellulose diacetate spinning dope having the following composition:

Dope concentration :	27.8% w/w solids
Dope viscosity :	115 Pa s (1150 poise) at 25°C
Water content :	3.1%
Acetyl value of flake :	54.8
Flake viscosity :	100 mPa s (100 centipoise) at 6% concentration
Amount of photochromic compound :	0.25 w/w dope

The dope was agitated by rolling for 24 hours to ensure complete mixing. Fibre was spun from the dope using conventional dry spinning techniques. The dope was maintained at a temperature of 60°C and was pumped through a 42 hole x 50 micrometres spinneret at a rate of 12 mls/min. The fibre was spun into a drying cell having an upper cell temperature of 60°C and a lower cell temperature of 100°C and an air flow of 0.57 m³ (20 standard cubic feet) per minute. The resulting yarn was taken up at a speed of 200 m/min on a cheesewinder. Between the take-up godet and the cheesewinder the yarn was interlaced using an air jet. The resulting yarn was 167(42) (decitex 167, no. of filaments 42), and was a very pale yellow with a shiny appearance. A matt yarn can be produced by adding titanium dioxide to the spinning dope.

Example 2

A solution of photochromic compound was prepared by dissolving 0.4g of the spiropyran 1',3',3'-trimethylindolino-6-nitrobenzospirropyran in 50ml acetone. The mixture was shaken for 1 hour.

The solution was then added to 1.4kg of cellulose acetate spinning dope having the same composition

as that described in Example 1, and blended for 24 hours by rolling.

A 167 (42) yarn was spun from the dope using the same spinning conditions as described in Example 1. The resulting yarn was a very pale pink colour with a bright appearance.

Example 3

The photochromic yarn as produced in Example 1 was woven together with a cellulose diacetate yarn known as Dixel (Registered Trade Mark), available from Courtaulds Fibres Ltd., into a fabric. The fabric had a 1 and 3 broken twill construction. The warp yarn was solely Dixel, and the weft yarn was a combination of photochromic yarn (1 over 6mm) and Dixel, each photochromic region consisting of 20 picks photochromic yarn.

The resulting fabric was slit into a number of labels measuring 40mm x 30mm. One of these labels is shown in Figures 1A and 1B. In visible light, before irradiation with UV light, the label 1 is completely white as shown in Figure 1A and the photochromic threads could not be seen. After irradiation with UV light for 20 seconds magenta-coloured stripes 2 appeared where the photochromic yarn had been woven in, as shown in Figure 1B. The stripes were each approximately 7mm in width and ran along the length of the label 1 in the weft direction. Subsequent irradiation with white light for 30 seconds caused the photochromic compound to revert to its near colourless form and the magenta stripes 2 disappeared, the label 1 again having the plain white appearance as shown in Figure 1A.

Example 4

The photochromic yarn as produced in Example 1 was woven into a fabric as described in Example 3 except that the weft yarn was a combination of photochromic yarn (1 over 50mm) and Dixel, and each photochromic region consisted of only one single pick of photochromic yarn.

The resulting fabric was slit into a number of labels measuring 50mm x 30mm. One of these labels is shown in Figures 2A and 2B. In visible light, before being irradiated with UV light, the label 10 appears completely white. After irradiation with UV light for 20 seconds the photochromic thread was clearly seen as a single magenta-coloured line 12 against the white background as shown in Figure 2B. After subsequent irradiation for 30 seconds with white light the magenta line disappeared and the label once more was completely white.

Example 5

The photochromic yarn as produced in Example 2 was woven into a fabric and the fabric slit into labels as described in Example 4.

After irradiation of a label with UV light the single photochromic thread was clearly seen as a purple line against a white background. After subsequent irradiation with white light the photochromic compound reverted to its near colourless state and the photochromic thread was no longer visible.

Example 6

The photochromic yarn as produced in example 1 was woven together with polyester yarn into a fabric. The warp was solely 76 (24) polyester and the weft was a combination of 167 (30) polyester with 4 picks of the photochromic yarn inserted every 200mm.

After irradiation of the fabric with UV light for 30 seconds magenta-coloured stripes appeared, each measuring approximately 2 mm in width. After subsequent irradiation with white light for 20 seconds the photochromic compound reverted to its near colourless state and the stripes were no longer visible.

Claims

1. A security device comprising woven material containing one or more threads of photochromic yarn, the yarn being substantially colourless when irradiated with visible light and reversibly converting to a coloured state when irradiated with UV light.

2. A security device as claimed in claim 1, which is in the form of a label.

3. A security device as claimed in claim 1 or 2, wherein the photochromic yarn is woven into the woven material.

4. A security device as claimed in any preceding claim, wherein the device comprises one thread of photochromic yarn incorporated in the woven material.

5. A security device as claimed in any preceding claim, wherein the photochromic yarn comprises cellulose acetate fibre having photochromic compound incorporated therein.

6. A security device as claimed in claim 5, wherein the photochromic compound is a spiropyran or a spiro-oxazine.

7. A security device as claimed in claim 5, wherein the photochromic compound is a fulgide or fulgimide.

8. The use of one or more threads of photochromic yarn as a security device in woven material, the yarn being substantially colourless when irradiated with visible light and reversibly converting to a coloured state when irradiated with UV light.

9. The use as claimed in claim 8, wherein the woven material is a label.

10. The use as claimed in claim 8, wherein the woven material is a textile piece good and a thread of photochromic yarn is woven into an edge thereof.

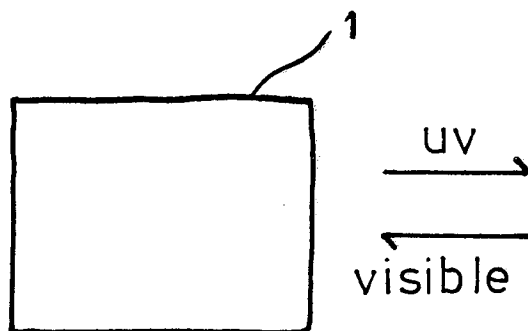


FIG. 1A

UV
→
←
visible

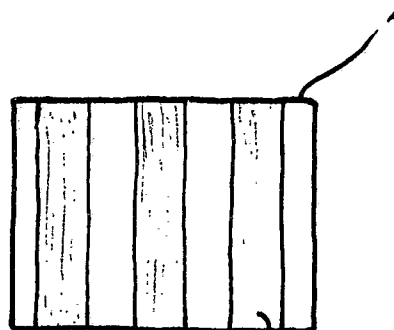


FIG. 1B

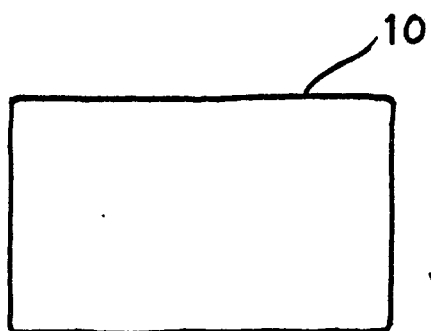


FIG. 2A

UV
→
←
visible

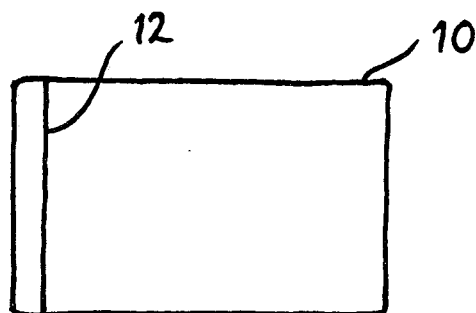


FIG. 2B



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,Y	GB-A-1 600 615 (PLESSEY CO. LTD) * Claims; page 5, lines 25-29; example 1 *	1,5	D 06 Q 1/00 D 03 D 15/00
D,X	FR-A-1 588 282 (COMPAGNIE DE SAINT-GOBAIN) * Claims; page 1, lines 4-8,22-25; page 2, lines 36-42; page 4, lines 3-41 *	1,3,4,6,8	
A	GB-A- 423 281 (RECHT) * Claims; page 2, lines 67-96 *	1,10	
Y	EP-A-0 169 750 (JALON) * Claims; page 1, line 1 - page 2, line 16; page 6, lines 19-30 *	1,8	
D,A	WPIL FILE SUPPLIER, no. 86-249926/38, Derwent Publications Ltd, London, GB; & JP-A61 179 399 (OKURASHO INSATSU KY) 12-08-1986 * Abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			D 06 Q D 03 D D 21 H D 04 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24-05-1989	Examiner HELLEMANS W.J.R.
CATEGORY OF CITED DOCUMENTS 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 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			