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

(19) World Intellectual Property Organization

International Bureau



(43) International Publication Date 22 December 2005 (22.12.2005)

PCT

(10) International Publication Number WO 2005/120855 A1

(51) International Patent Classification⁷: 15/10

B42D 15/00,

(21) International Application Number:

PCT/GB2005/002271

(22) International Filing Date: 9 June 2005 (09.06.2005)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0412979.7

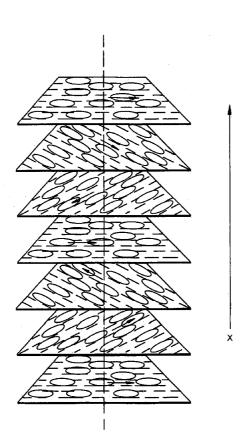
10 June 2004 (10.06.2004) GE

(71) Applicant (for all designated States except US): DE LA RUE INTERNATIONAL LIMITED [GB/GB]; De La Rue House, Jays Close, Basingstoke, Hampshire RG22 4BS (GB).

- (72) Inventors; and
- (75) Inventors/Applicants (for US only): EASTELL, Christopher, John [GB/GB]; 12 Dunn Crescent, Kintbury, Berkshire, RG17 9UH (GB). COMMANDER, Lawrence, George [GB/GB]; 7 Edenhall Close, Tilehurst, Reading, RG31 6RR (GB).
- (74) Agents: BUCKS, Teresa, Anne et al.; Boult Wade Tennant, Verulam Gardens, 70 Gray's Inn Road, London WC1X 8BT (GB).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: IMPROVEMENTS IN SECURITY DEVICES



(57) Abstract: The present invention relates to improvements in security devices that can be used in varying shapes and sizes for various authenticating or security applications, particularly a device which on the application of heat uses a shape memory polymer material to induce a colourshift in a liquid crystal The invention therefore relates to a security substrate (10) comprising a polymeric liquid crystal material (13) and a shape memory polymer film (14), wherein the application of a predetermined external stimuli to the substrate (10) which causes the shape memory polymer film (14) to change shape which, in turn causes the liquid crystal material (13) to stretch or contract and thereby induce in the liquid crystal material (13) a temporary colour change.

WO 2005/120855 A1



(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO,

NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— of inventorship (Rule 4.17(iv)) for US only

Published:

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

IMPROVEMENTS IN SECURITY DEVICES

The present invention relates to improvements in security devices that can be used in varying shapes and sizes for various authenticating or security applications, particularly a device which on the application of heat uses a shape memory polymer material to induce a colourshift in a liquid crystal material.

5

10 The increasing popularity of colour photocopiers and other imaging systems and the improving technical quality of colour photocopies has led to an increase in the counterfeiting of banknotes, passports, and identification cards etc. There is, therefore, a need to add additional authenticating or security features to 15 existing features. Steps have already been taken to introduce optically variable features which cannot be reproduced by a photocopier into such documentation. There is also a demand to introduce features which are discernible by the general public but which are 20 "invisible" to, or viewed differently, by a photocopier. Since a photocopying process typically involves scattering high-energy light off an original document containing the image to be copied, one solution would be to incorporate one or more features into the document 25 which have a different perception in reflected and transmitted light, an example being watermarks and enhancements thereof.

30 It is known that certain liquid crystal materials exhibit a difference in colour when viewed in

transmission and reflection as well as an angularly dependent coloured reflection. Liquid crystal materials have been incorporated into documents, identification cards and other security elements with a view to creating distinctive optical characteristics. EP-A-0435029 is concerned with a data carrier, such as an identification card, which comprises a liquid crystal polymer layer or film in the data carrier. The liquid crystal polymer is in solid form at room temperature and is typically within a laminate structure. The intention is that the liquid crystal layer, which is applied to a black background, will demonstrate a high degree of colour purity in the reflected spectrum for all viewing angles. Automatic testing for verification of authenticity is described using the wavelength and polarisation properties of the reflected light in a single combined measurement. This has the disadvantage of being optically complex using a single absolute reflective measurement requiring a uniform liquid crystal area on a black background.

20

25

30

5

10

15

AU-A-488652 is also concerned with preventing counterfeit copies by introducing a distinctive optically variable feature into a security element. This patent specification discloses the use of a liquid crystal "ink" laminated between two layers of plastic sheet. The liquid crystal is coated on a black background so that only the reflected wavelengths of light are seen as a colour. The patent is primarily concerned with liquid crystals which have the characteristic of changing colour with variation in temperature.

3

PCT/GB2005/002271

WO-A-03061980 discloses a method for manufacturing a security substrate, which combines the use of demetallised indicia with the colourshift effect of liquid crystal materials. According to WO-A-03061980 there is provided a method of manufacturing a substrate comprising the steps of applying a darkly coloured resist to at least a part of a metallic layer on one side of a substantially transparent polymeric film, removing metal from areas not covered by the resist to form demetallised regions and applying a polymeric liquid crystal material over the resist and the demetallised regions. The substrate produced by the method in WO-A-03061980 can be incorporated into secure documents such as banknotes as a thread, stripe or patch.

15

20

25

30

5

10

WO 2005/120855

EP-A-1281538 discloses an optically variable marking comprising a semi-opaque substrate with a first surface that is covered with a liquid crystal polymer layer, and a second surface that is partially covered with a metal layer in the shape of a pattern. If the marking is viewed in reflection the device looks uniform and the reflective colour of the liquid crystal is seen. In transmission the pattern in the metal layer is visible through the semi-opaque substrate and the transmitted light is of a different colour to the reflected light.

Cholesteric liquid crystals have certain unique properties in the chiral nematic phase. It is the chiral nematic phase that produces an angularly dependent coloured reflection and a difference in colour when viewed in either transmission or reflection. Cholesteric liquid crystals form a helical structure which reflects

circularly polarised light over a narrow band of wavelengths. The wavelength is a function of the pitch of the helical structure which is formed by alignment within the liquid crystal material. An example of such a structure is depicted in Figure 1 with the cholesteric helical axis in the direction of the arrow X. The reflection wavelength can be tuned by appropriate choice of chemical composition of the liquid crystal. The materials can be chosen to be temperature sensitive or insensitive. Both handednesses of circularly polarised light can be reflected by choice of the correct materials and thus high reflectivities at specific wavelengths can be achieved with double layers of liquid crystals. The wavelength of reflected light is also dependent on the angle of incidence, which results in a colour change perceived by the viewer as the device is tilted (Figure 2).

5

10

15

20

25

30

On a dark background, only the reflective effect is observed, since little light is being transmitted from behind. When the dark background is removed or not present and the device is viewed in transmission, the intensity of the transmitted colour swamps the reflective colour. Of the light which is not reflected, a small proportion is absorbed and the remainder is transmitted through the liquid crystal material 3. When correctly configured there is a dramatic change between the transmitted colour in the direction of arrow Y and reflected colour in the direction of arrow Z (Figure 3). The region on either side of the liquid crystal layer 3 in Figure 3 is a transparent polymer or glass. To achieve this effect the area of the substrate which is occupied by the liquid crystal must be transparent or translucent.

The transmitted and reflected colours are complementary, for example, a green reflected colour produces a magenta transmitted colour.

An interesting property of cholesteric liquid 5 crystal materials is that a mechanical deformation of the liquid crystal material through the application of a stress can cause a shift of the reflection band and therefore a change in colour of the liquid crystal material. The effect of stress on cholesteric liquid 10 crystal materials has been reported in the Journal of Advanced Materials (Adv. Mater. 2001, 13, No.14, July 18). The use of liquid crystals in security devices to generate a piezochromic effect (i.e. a reversible colour change under the action of a pressure) is known and has 15 been disclosed in FR-A-2698390. FR-A-2698390 describes a security thread comprising a piezochromic liquid crystal layer in which a colour change is induced by the authenticator pressing down on selected areas of the 20 thread. The effectiveness of the device is dependent on the amount of pressure applied by the authenticator which can lead to unwanted variability in the degree of colour change observed.

The object of the security device of the present invention is to induce a known, controlled amount of stress in a liquid crystal polymer, independent of the authenticator, such that the observed colourshift is always identical. This is achieved by combining a liquid crystal film with a shape memory polymer film in a 30 laminate construction. The application of body heat by touch results in a controlled stretch in the shape memory

polymer film that induces a known stress in the liquid crystal film. The induced stress in the liquid crystal film causes a shift in the reflection band and a change in the observed colour. On removal of the heat the elastic nature of the laminate system will return the shape memory polymer to its original shape and the liquid crystal film to its original colour. The device offers increased security over the traditional liquid crystal thread by exhibiting both an angular dependent colour change and a touch-sensitive colour change.

Shape memory polymers (SMP) have the property of being able to change their shape, from a temporary shape to a permanent shape, on the application of an external stimulus such as temperature. Materials exhibiting this property have been disclosed in US-B-6720402 and US-B-6160084.

The SMP's can include at least one hard segment and at least one soft segment, or can include at least one kind of soft segment wherein at least one kind of the soft segments are crosslinked, without the presence of a hard segment. The term "segment" refers to a block or sequence of polymer forming part of the SMP. The terms hard segment and soft segment are relative terms, relating to the softening point (melting point or glass transition temperature) of the segments. The hard segment(s) has a higher softening point than the soft segment(s).

5

10

SMP's can be thermoplastic, thermoset, interpenetrating networks, semi-interpenetrating networks, or mixed networks. Polymers can be a single polymer or a blend of polymers. Polymers can be linear, branched, thermoplastic elastomers with side chains or any kind of dendritic structural elements. Stimuli causing shape change can be temperature, ionic change, pH, visible irradiation, UV irradiation, electric field, magnetic field or ultrasound.

10

15

20

5

Thermoplastic SMP's are generally characterised as phase segregated block co-polymers comprising a hard segment and a soft segment. The hard segment is typically crystalline, with a defined melting point, and the soft segment is typically amorphous, with a defined glass transition temperature. In some embodiments, however, the hard segment is amorphous and has a glass transition temperature rather than a melting point. In other embodiments, the soft segment is crystalline and has a melting point rather than a glass transition temperature. The melting point or glass transition temperature of the soft segment is substantially less than the melting point or glass transition temperature of the hard segment.

When the thermoplastic SMP is heated above the melting point or glass transition temperature of the hard segment, the material can be shaped. This (original) shape can be memorized by cooling the SMP below the melting point or glass transition temperature of the hard segment. When the shaped SMP is cooled below the melting point or glass transition temperature of the soft segment while the shape is deformed, that (temporary) shape is

fixed. The original shape is recovered by heating the material above the melting point or glass transition temperature of the soft segment but below the melting point or glass transition temperature of the hard segment.

5

10

15

20

25

30

One example of a thermosetting SMP system is a polymer network prepared by covalently cross-linking macromonomers, i.e. polymers which contain polymerisable endgroups such as carbon-carbon double bonds. The polymerisation process can be induced by using light or heat sensitive initiators or by curing with ultra violet light. Thermoset SMP's can be prepared by extruding the pre-polymerized material (macromonomers), and fixing the original shape at a temperature above the T_{trans} (melting point or glass transition temperature) of the thermoset polymer, for example, by photocuring reactive groups on the macromonomer. The temporary shape is fixed by cooling the material below T_{trans} after deforming the material. The original shape is recovered by heating the material above the T_{trans} of the thermoset polymer and thereby cleaving the cross-links. Alternative thermoset SMP systems, such as those described in Nature vol 434, page 879, 14th April 2005, exist where the cross-links are cleaved, and therefore the shape change is induced, by UV irradiation.

Examples of polymer segments that can be used in SMP systems are detailed in US-B-6720402. SMP systems particularly suitable for this invention include, but are not limited to, polyamides, polyester amides, poly(amino acid)s, synthetic poly(amino acids), polyanhydrides, polycarbonates, polycarpolactones, polyacrylates,

polyalkylenes, polyacrylamides, polyalkylene glycols, polyalkylene oxides, polyalkylene terephthalates, polyortho esters, polyvinyl ethers, polyvinyl esters, polyvinyl halides, polyvinylpyrrolidone, polyesters, polylactides, polyglycolides, polysiloxanes, polyurethanes, ethylene vinyl acetate, poly(meth)acrylic acid, polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyvinylphenol, and copolymers and mixtures thereof.

10

15

30

5

US-A-2004014929 discloses that it is possible to blend certain SMP compositions with other commercially available polymers, such as polyolefins, in particular polyethylene and polypropylene, or vinyl polymers, such as polystyrene and PVC. It could be shown that with a content of from 50 to 90 wt-% of SMP, the shape memory properties could be retained. This enables in particular the preparation of low cost SMP materials.

20 SMP's suitable for use in the current invention can be produced as a film or as a coating and therefore can be combined in a straightforward manner with a colourshifting liquid crystal film or coating to produce a multilayer security device suitable for incorporation into a document of value.

The invention therefore provides a security substrate comprising a polymeric liquid crystal material and a shape memory polymer film, wherein the application of a predetermined external stimuli to the substrate which causes the shape memory polymer film to change shape which, in turn causes the liquid crystal material

to stretch or contract and thereby induce in the liquid crystal material a temporary colour change.

The invention also provides a method of manufacturing a security substrate comprising the application of a layer of polymeric liquid crystal material to a carrier layer of a polymeric film, applying a layer of shape memory polymer film, wherein the shape memory polymer film has first been stretched along one of its dimensional axes whilst being heated to above melting point or a glass transition temperature of a hard segment of the shape memory polymer and subsequently cooled under tension to a temperature below the melting point or glass transition temperature of the hard segment, but above the melting point or glass transition temperature of a soft 15 segment of shape memory polymer, and further cooling the film to below the melting point or glass transition temperature of the soft segment whilst the tension is released.

20

25

30

10

The invention further provides a method of manufacturing a security substrate comprising the application of a layer of polymeric liquid crystal material to a layer of shape memory polymer film, wherein the shape memory polymer film has first been stretched along one of its dimensional axes whilst being heated to above melting point or a glass transition temperature of a hard segment of the shape memory polymer and subsequently cooled under tension to a temperature below the melting point or glass transition temperature of the hard segment, but above the melting point or glass transition temperature of a soft segment of shape memory polymer, and further cooling the film to below the

melting point or glass transition temperature of the soft segment whilst the tension is released.

Preferred embodiments of the present invention will now be described, by way of example only with reference to the accompanying drawings in which:

Figure 1 depicts chiral nematic alignment of a cholesteric liquid crystal material;

10 Figure 2 shows how the reflection from a cholesteric liquid crystal material varies with the angle of incidence;

Figure 3 depicts the transmission and reflection of light incident on a liquid crystal material;

15 Figure 4 is a cross-sectional side elevation of a substrate according to the present invention for use in security or authenticating devices.;

20

Figures 5 to 8 are cross-sectional side elevations of alternative embodiments of the substrate of Figure 4; and

Figures 9 and 10 are cross-sectional side elevations of machine readable constructions incorporating a substrate according to the present invention.

25 Referring to Figure 4, the substrate 10 comprises a transparent polymeric film 11. Suitable polymeric films are for example those made from polyethylene terephthalate (PET) which are commercially available from Dupont under the trade name Melinex. A black or dark pigmented ink or coating 12 is then applied to one surface of the polymeric film 11 in order to visually

accentuate the colour change of the liquid crystal material 13. The coating 12 may be applied, by a number of techniques using, for example, a roll coater or alternatively using a printing press by flexographic,

5 offset lithographic or gravure techniques. Alternatively a black or dark dye can be applied to the surface of the polymeric film 11. The black or dark coating/dye may be a conducting material, such as carbon black, to produce a machine-readable conducting layer. Alternatively it may be a magnetic material, such as magnetite, to produce a machine-readable magnetic layer.

Whilst the use of a black, or dark coating/dye may give rise to the strongest colour shift effects, other effects may be generated by the use of a dyed resist of other colours or a combination of colours giving rise to differing apparent colour shift colours.

then coated, transferred or laminated on top of the coated polymeric film 11. A layer of a suitable adhesive (not shown in Figure 4) may be required for this process, applied between the black/dark coating 12 and the liquid crystal layer 13. A transparent or translucent SMP polymer film 14 is then transferred or laminated to the surface of the liquid crystal film 13. A layer of a suitable adhesive (not shown in Figure 4) may be required for this process, applied between the liquid crystal layer 13 and the SMP layer 14.

PCT/GB2005/002271

The SMP layer 14 will be applied or transferred to the liquid crystal film 13 in its temporary shape, which will have been fixed during the initial forming stages of the SMP film 14. In a preferred method a thermoplastic polymer system is used for the SMP film 14 which can be produced by known polymer film production processes, such as the blown film process, the cast film process and the tentering process. For example during production the SMP film 14 is heated above the melting point or glass transition temperature of the hard segment. The film 14 is then cooled below the melting point or glass transition temperature of the hard segment. During the cooling process the film 14 is kept under tension along one of its dimensional axes in order to fix the permanent "stretched" shape. The film 14 is then cooled below the melting point or glass transition temperature of the soft segment, while the tension is released, fixing a temporary shape which has contracted along one of its dimensional axes relative to the permanent shape. The "stretched" shape can then be recovered by heating the material above the melting point or glass transition temperature of the soft segment but below the melting point or glass transition temperature of the hard segment.

25

30

20

5

10

15

The activation temperature, i.e. the melting point or glass transition temperature of the soft segment, at which the film 14 switches from its temporary shape to its permanent shape can be controlled by changing the composition of the hard and soft segments. For the current invention the activation temperature is in the range 25°C to 80°C, preferably 30°C to 50°C. In a preferred

embodiment the material can be formulated such that the switch from the temporary shape to the permanent shape occurs at body temperature, $\sim 35-37^{\circ}\text{C}$, and therefore can be activated by touch.

5

10

15

20

25

For the purpose of this illustration the SMP film 14 in Figure 4 has a temporary shape which has been formed by a 1% contraction of the permanent "stretched" shape in one of its dimensional axes in the plane of the film. When the substrate in Figure 4 is viewed through the transparent or translucent SMP film in its temporary shape a highly visible colour shift effect is observed from the liquid crystal layer 13 as the device 10 is tilted. For example the colour shift can be from red, when viewed at a normal angle of incidence to the plane of substrate, to green when viewed at a low angle of incidence to the plane of the substrate. On warming the security device above the activation temperature, preferably 35-37°C, the shape memory polymer 14 reverts to its "stretched" permanent shape and induces a stress in the liquid crystal film 13. The induced stress in the liquid crystal film 13 produces a known colour change. In this example the liquid crystal film 13 is stretched and the colour goes to shorter wavelengths for example red goes to green and green goes to blue, resulting in a colour shift from green to blue as the substrate 10 is tilted in its stretched state.

On removal of the heat the elastic nature of the laminate system will force the substrate 10 to relax to its original dimension and the liquid crystal film 13 to its original colour. This will result in the SMP film 14

reverting to the "unstretched" temporary shape and therefore the authentication process is reversible.

The change in colourshift when the substrate 10 is

warmed is dependent on the stress induced in the liquid crystal film 13 by the shape change in the SMP film 14.

Different colour shifts can be achieved by varying the degree of shape change and the amount of contraction and expansion in the SMP film 14. In addition the contraction and or expansion can occur along one or more dimensional axes depending how the SMP film 14 is formed.

In an alternative construction the position of the liquid crystal polymer layer 13 and the SMP film 14 are reversed such that the SMP polymer film 14 is applied to the black/dark coating 12. The functionality of the device is not significantly affected by this alteration. It is also possible to replace the polymeric carrier film 11(for example PET) with a SMP film 14 such that a separate SMP film layer 14 is no longer required, as shown in Figure 5.

15

20

In a further modification of the construction shown in Figure 5 a second SMP film, with the same

25 characteristics as SMP film 14, is laminated on top of the liquid crystal film such that the liquid crystal film is sandwiched between the two shape memory polymer films. This construction minimises any unwanted bending of the laminate system arising from the liquid crystal material being stretched to a different extent than the SMP.

It is also possible that the liquid crystal polymer is one of the polymer segments of the shape memory polymer such that a single material layer can be formed which exhibits the properties of the both the liquid crystal polymer and the shape memory polymer. For example for the construction shown in figure 4 the liquid crystal layer 13 and the SMP layer 14 may be replaced by a single layer of material which exhibits both their characteristics. A combined liquid crystal/SMP layer could also be achieved by blending the liquid crystal material with the SMP.

10

30

Figure 6 shows a further embodiment of the substrate of the present invention. The structure is the same as 15 that shown in Figure 4 except in that the combination of a transparent polymeric film 11 with a black/dark coating 12 has been replaced with a semi-opaque polymeric film 15. This is preferably a plastic film that is darkened, for example to about 95% absorbance, by incorporation of 20 light absorbing particles like, for example, carbon black. The semi-opaque film 15 has the same function as the black/dark coating 12 in Figure 4 which is to visually accentuate the colour change of the liquid crystal material 13. The overall function and appearance 25 of the substrate in Figure 6 is otherwise the same as that discussed with reference to Figure 4.

Figure 7 shows a further embodiment of the substrate 10 of the current invention. The structure is the same as that shown in Figure 6 except that the opposite surface of the semi-opaque polymeric film 15 has been metallised, using vapour deposited aluminium 16, and

contains demetallised indicia 17, produced by a method, such as that described in EP-A-0319157. Alternatively the vapour deposited metallised layer can be replaced with conducting or non-conducting metallic ink.

5

10

15

20

25

30

When the substrate 10 of Figure 7 is viewed in reflection through the transparent or translucent SMP film 14 in its temporary shape a highly visible colour shift effect is observed from the liquid crystal layer 13 as the substrate 10 is tilted. For example the colour shift can be from red, when viewed at a normal angle of incidence to the plane of substrate 10, to green when viewed at a low angle of incidence to the plane of the substrate 10. When the substrate 10 is viewed in transmission the demetallised indicia 17 becomes visible and the transmitted light will be of a complementary colour to the reflected light. In this example when viewed normally the main body of the substrate 10 will appear red due to the reflected light but the demetallised indicia 17 will appear green from the transmitted light. On warming the security substrate 10 above the activation temperature, preferably $35-37^{\circ}\text{C}$, the SMP film 15 reverts to its "stretched" permanent shape and induces a stress in the liquid crystal film 13. The induced stress in the liquid crystal film 13 produces a known colour change. In this example the liquid crystal film 13 is stretched and when viewed in reflection the colour goes to shorter wavelengths for example red goes to green and green goes to blue, resulting in a colour shift from green to blue as the substrate 10 is tilted in its stretched state. The colour of the demetallised indicia 17, when viewed in transmission, will also change in this case from green to red. On removal of the heat the elastic nature of the laminate system will force the substrate 10 to relax to its original dimension and the liquid crystal film 13 to its original colour.

5

10

15

20

25

30

Figure 8 illustrates a further embodiment of the substrate 10 of the present invention for use in security or authenticating devices. The structure shown is a combination of a SMP film 14 with an existing approach for the manufacture of liquid crystal security substrates disclosed in WO-A-03061980. The substrate 10 comprises a transparent polymeric film 11 which has been metallised using for example vapour deposited aluminium. Suitable polymeric films are for example those made from polyethylene terephthalate (PET) which are commercially available from Dupont under the trade name Melinex. The metal layer 16 is printed with a resist 18 which contains a black or dark dye or pigment. The printed metallised film 11 is then partially demetallised, according to a known demetallisation process using a caustic wash which removes the metal in the regions not printed with the resist 18. The remaining regions coated with the resist provide a black layer which is visible when the demetallised film 19 is viewed from a first side (along arrow Y) interspersed with clear regions. The shiny metal of the remaining parts of the metallised layer 16 are only visible from an opposite side of the demetallised film 19 (along arrow X). The resist 18 may be printed in the form of the indicia such as words, numerals, patterns and the like; in which case the resulting indicia will be positively metallised, with the metal still covered by the dark or black resist 18. Alternatively the resist 18 may be printed so as to form indicia negatively, in which

case the resulting indicia will be provided by the demetallised regions 17. The indicia, however formed, are clearly visible from both sides, especially in transmitted light, due to the contrast between the regions of the metal which have been removed and the remaining opaque regions. The black or dark resist may be loaded with a conducting pigment, such as carbon black, to produce a machine-readable conducting layer.

Alternatively it may be loaded with a magnetic material, such as magnetite, to produce a machine-readable magnetic layer.

A layer of polymeric liquid crystal material 13 is then coated, transferred or laminated to the demetallised film 19 over the remaining parts of the black resist layer 18 and the demetallised regions 17. A layer of a suitable adhesive may be required, for this process, applied between the black resist layer and the liquid crystal layer (not shown in Figure 8). A transparent or translucent SMP film 14 is then transferred or laminated to the surface of the liquid crystal film 13. A layer of a suitable adhesive (not shown in Figure 8) may be required, for this process, applied between the liquid crystal layer 13 and the SMP layer 14.

25

30

20

5

10

15

For the purpose of this illustration the SMP film 14 in Figure 8 has a temporary shape which has been formed by a 1% contraction of the permanent "stretched" shape in one of its dimensional axes in the plane of the film 14. When the substrate 10 is viewed in reflection through the transparent or translucent SMP film 14 in its temporary shape a highly visible colour shift effect is observed

from the regions of the liquid crystal layer 13 located above the dark as the substrate 10 is tilted. For example the colour shift can be from red, when viewed at a normal angle of incidence to the plane of substrate, to green when viewed at a low angle of incidence to the plane of the substrate 10. Additionally clear positive or negative indicia 17 can be seen in transmission from either side.

On warming the substrate 10 above the activation 10 temperature, preferably 35-37°C, the shape memory polymer film 14 reverts to its "stretched" permanent shape and induces a stress in the liquid crystal film 13. The induced stress in the liquid crystal film 13 produces a known colour change. In this example the liquid crystal 15 film 13 is stretched and when viewed in reflection the colour goes to shorter wavelengths for example red goes to green and green goes to blue, resulting in a colour shift from green to blue as the device is tilted. On removal of the heat the elastic nature of the laminate 20 system will force the substrate 10 to relax to its original dimension and the liquid crystal film 13 to its original colour.

The substrate 10 of the current invention can be

slit or cut into patches, foils, stripes, strips or
threads for incorporation onto or into plastic or paper
substrates in accordance with known methods. Whilst these
are preferably partially embedded into a paper or plastic
substrate, they may be applied to a substrate or wholly

embedded within.

It will be further understood by those skilled in the art that the substrate of the present invention could be used in combination with existing approaches for the manufacture of security threads. Examples of suitable constructions that can be used include, but are not limited to, those cited within EP-A-0516790, WO-A-9825236, and WO-A-9928852.

10

15

20

25

Figure 9 shows a machine readable construction laminated to a SMP film 14. The machine-readable construction comprises a metallised PET base layer 11 which is demetallised with a suitable design ensuring "tramlines" 20 of metal are left along each edge of the security thread 21. As described above a black resist 18 is used during the demetallisation process. On to a black resist 18 an optional protective layer 22 may be applied prior to application of a magnetic layer 23. A suitable protective layer 22 is VHL31534 supplied by Sun Chemical applied with a coat weight of 2gsm. The protective layer 22 may optionally be pigmented. A layer of polymeric liquid crystal material 13 is then coated, transferred or laminated to the demetallised film 19 over the magnetic layer 23 and the remaining parts of the black resist layer 18 and the demetallised regions. A layer of a suitable adhesive may be required (not shown in Figure 9), for this process, applied between the black resist layer 18 and the liquid crystal layer 13.

A transparent or translucent SMP film 14 is then 30 transferred or laminated to the surface of the liquid crystal film 13. A layer of a suitable adhesive (not shown in Figure 9) may be required, for this process, applied between the liquid crystal layer 13 and the SMP layer 14.

is applied as tramlines along both edges of the device.

It should also be noted that the magnetic material 23 could be applied in any manner so long as it does not obscure the demetallised regions and consequently obscure the indicia 17. Figure 10 shows another preferred embodiment where the magnetic material 23 is applied over the resist 18 in a discontinuous manner to form blocks of magnetic material 23.

The functionality of the device 21 illustrated in Figure 9 is the same as that illustrated in Figure 8, except that it has a machine-readable component.

In addition to changing shape in response to changes

20 in temperature, the SMP's utilised in the current
invention can change shape in response to application of
light, electric field, magnetic field and/or ultrasound.

The security substrate of the current invention can
therefore also be produced such that it can be

25 authenticated using any of the above stimuli.

These examples are illustrative only and there are numerous other possibilities

CLAIMS:

5

10

15

- 1. A security substrate comprising a polymeric liquid crystal material and a shape memory polymer film, wherein the application of a predetermined external stimuli to the substrate which causes the shape memory polymer film to change shape which, in turn causes the liquid crystal material to stretch or contract and thereby induce in the liquid crystal material a temporary colour change.
 - 2. A security substrate as claimed in claim 1 wherein the shape of the shape memory polymer film changes shape when warmed to a temperature above an activation temperature.
 - 3. A security substrate as claimed in claim 1 wherein the shape of the shape memory polymer film changes shape when subjected to light.

- 4. A security substrate as claimed in claim 1 wherein the shape of the shape memory polymer film changes shape when subjected to an electric field.
- 25 5. A security substrate as claimed in claim 1 wherein the shape of the shape memory polymer film changes shape when subjected to a magnetic field.
- 6. A security substrate as claimed in claim 1
 30 wherein the shape of the shape memory polymer film changes shape when subjected to ultrasound.

7. A security substrate as claimed in any one of the preceding claims comprising separate layers of polymeric liquid crystal material and shape memory polymer film.

5

8. A security substrate as claimed in any one of claims 1 to 6 in which the polymeric liquid crystal material and shape memory polymer film are combined in a single layer.

- 9. A security substrate as claimed in any one of the preceding claims further comprising a carrier layer of a polymeric film.
- 15 10. A security substrate as claimed in claim 9 in which the carrier layer comprises the layer of shape memory polymer film.
- 11. A security substrate as claimed in claim 9 or 20 claim 10 in which the carrier layer incorporates a dark dye or colouring.
- 12. A security substrate as claimed in claim 9 or claim 10 in which a dark layer is applied to the carrier 25 layer.
 - 13. A security substrate as claimed in claim 12 in which the dark layer comprises a pigmented ink.
- 30 14. A security substrate as claimed in claim 12 in which the dark layer comprises a coating.

- 15. A security substrate as claimed in claim 2 or any of preceding claim dependent of claim 2 in which the activation temperature lies in the range of 25 to 80° C.
- 5 16. A security substrate as claimed in claim 15 in which the activation temperature lies in the range of 30 to 50° C.
- 17. A security substrate as claimed in claim 16 in which the activation temperature lies in the range of 35 to 37°C .
- 18. A security substrate as claimed in any of claims 9 to 17 in which the layer of liquid crystal15 material is sandwiched between the carrier layer and the layer of shape memory polymer film.
 - 19. A security substrate as claimed in any one of claims 9 to 17 in which the layer of shape memory polymer film is sandwiched between the carrier layer and the layer of liquid crystal material.

- 20. A security substrate as claimed in any of claims 9 to 17 in which the layer of liquid crystal25 material is sandwiched between the layer of shape memory polymer film and a further layer of shape memory polymer film.
- 21. A security substrate as claimed in any one of claims 9 to 20 in which the carrier layer is transparent or translucent.

- 22. A security substrate as claimed in any one of claims 9 to 21 in which the carrier layer is at least partially metallised.
- 5 23. A security substrate as claimed in claim 22 in which the carrier layer is at least partially metallised on a first surface and the liquid crystal material and shape memory polymer layers are applied to a second surface of the carrier layer.

10

15

- 24. A security substrate as claimed in claim 22 in which the carrier layer is at least partially metallised to form a metallic layer on a same side of the carrier layer to which the liquid crystal and shape memory polymer films are applied, at least some regions of the metallic layer being coated with a dark material.
- 25. A security substrate as claimed in any one of claims 22 to 24 in which indicia are formed by gaps in the partially metallised layer.
 - 26. A security substrate as claimed in any one of claims 22 to 24 in which metallised indicia are provided with gaps therebetween.

- 27. A security substrate as claimed in any one of claims 22 to 26 in which a metallic ink is applied to the carrier layer to form the partial metallisation.
- 28. A security substrate as claimed in any one of claims 22 to 26 in which the carrier layer is partially metallised by a metal deposition process.

29. A security substrate as claimed in any one of the preceding claims comprising a magnetic material beneath the liquid crystal and shape memory polymer layers.

5

- 30. A security substrate as claimed in any one of the preceding claims slit or cut to form a patch, foil, stripe, security element or security thread.
- 31. A security substrate as claimed in any one of the preceding claims in which the shape memory polymer is a thermoplastic polymer.
- 32. A security substrate as claimed in any one of claims 1 to 30 in which the shape memory polymer is a thermosetting polymer.
 - 33. A security material incorporating a security substrate as claimed in any one of the preceding claims.

- 34. A security article formed from a security material of claim 33, such as a banknote, passport, certificate or other document of value.
- 35. A method of manufacturing a security substrate comprising the application of a layer of polymeric liquid crystal material to a carrier layer of a polymeric film, applying a layer of shape memory polymer film, wherein the shape memory polymer film has first been stretched along one of its dimensional axes whilst being heated to
 - along one of its dimensional axes whilst being heated to above melting point or a glass transition temperature of a hard segment of the shape memory polymer and subsequently cooled under tension to a temperature below

the melting point or glass transition temperature of the hard segment, but above the melting point or glass transition temperature of a soft segment of shape memory polymer, and further cooling the film to below the melting point or glass transition temperature of the soft segment whilst the tension is released.

36. A method of manufacturing a security substrate comprising the application of a layer of polymeric liquid crystal material to a layer of shape memory polymer film, wherein the shape memory polymer film has first been stretched along one of its dimensional axes whilst being heated to above melting point or a glass transition temperature of a hard segment of the shape memory polymer and subsequently cooled under tension to a temperature below the melting point or glass transition temperature of the hard segment, but above the melting point or glass transition temperature of a soft segment of shape memory polymer, and further cooling the film to below the melting point or glass transition temperature of the soft segment whilst the tension is released.

10

15

- 37. A method as claimed in claims 35 or 36 further comprising the step incorporating a dark dye or colouring in the carrier layer or the layer of shape memory polymer film.
- 38. A method as claimed in claim 35 or claim 36 further comprising the step of applying a dark layer to the carrier layer or the layer of shape memory polymer film, beneath the polymeric liquid crystal layer.

WO 2005/120855 PCT/GB2005/002271 29

39. A security substrate substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

. ...

1/6

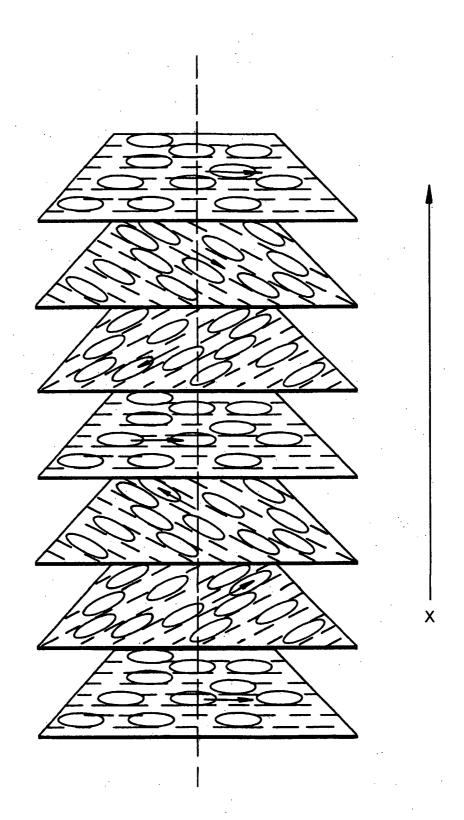
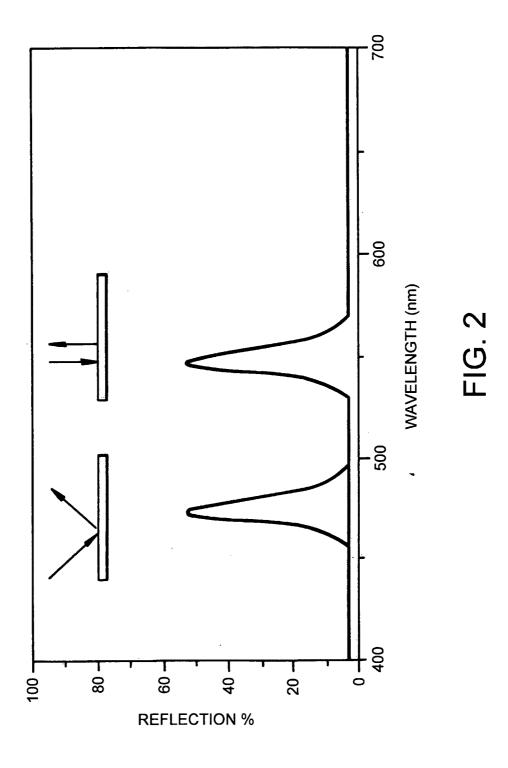


FIG. 1



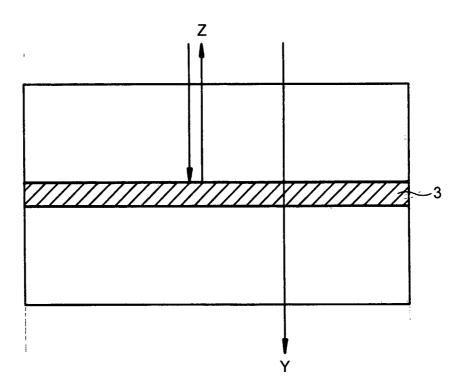


FIG. 3

4/6

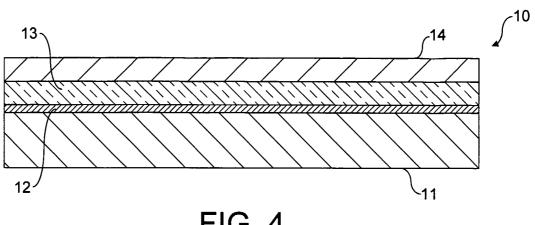
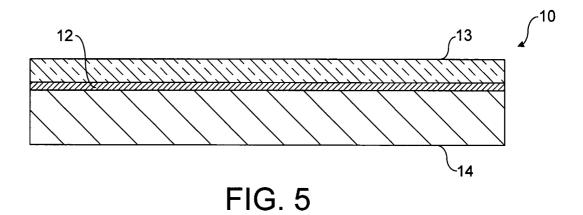
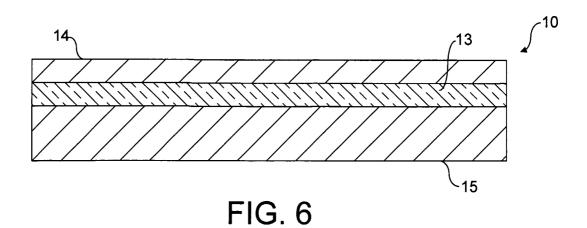
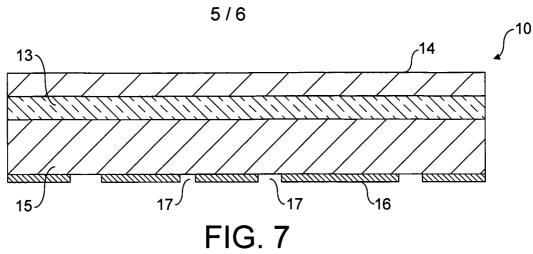
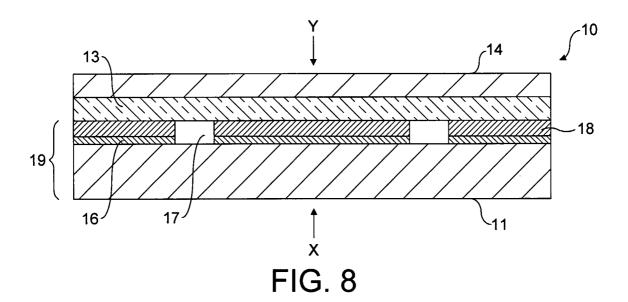


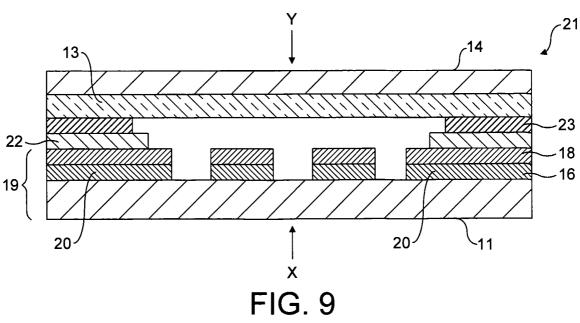
FIG. 4

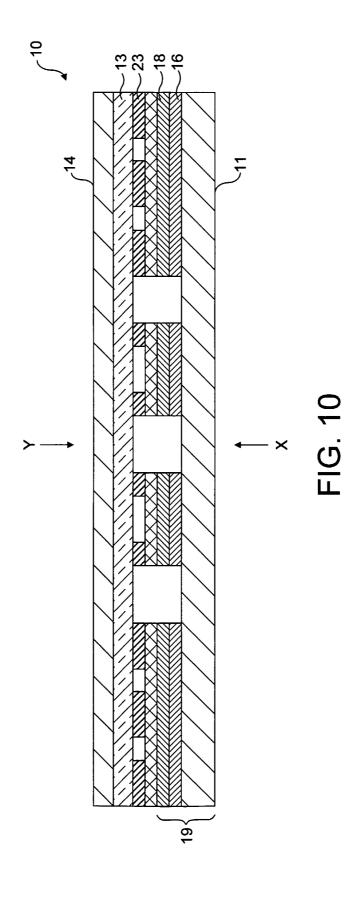












INTERNATIONAL SEARCH REPORT

al Application No PCT/GB2005/002271

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B42D15/00 B42D15/10

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

B. FIELDS SEARCHED

 $\frac{\text{Minimum documentation searched (classification system followed by classification symbols)}}{IPC~7~G02B~B42D~B41M}$

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

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

EPO-Internal, WPI Data, PAJ

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 05, 3 May 2002 (2002-05-03) & JP 2002 006280 A (DAINIPPON INK & CHEM INC), 9 January 2002 (2002-01-09) abstract	1,2,7,9, 12,15, 19,30, 33,34
X	EP 0 353 650 A (MITSUBISHI JUKOGYO KABUSHIKI KAISHA) 7 February 1990 (1990-02-07) page 6	1,2,8
Α	FR 2 698 390 A (ARJO WIGGINS SA) 27 May 1994 (1994-05-27) cited in the application claims 1-4	1,33-36

X Further documents are listed in the continuation of box C.	χ Patent family members are listed in annex.		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 15 September 2005	Date of mailing of the international search report 23/09/2005		
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Curt, D		

INTERNATIONAL SEARCH REPORT

Inte al Application No PCT/GB2005/002271

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT								
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.						
А	EP 0 701 231 A (SINGER, ANDREAS) 13 March 1996 (1996-03-13)	1,2, 15-17, 33-36						
	the whole document							
								
,		·						
	·							
-								
<u>'</u>								

INTERNATIONAL SEARCH REPORT

Inte al Application No PCT/GB2005/002271

	Publication date	Patent family member(s)		Publication date
Α	09-01-2002	NONE		
A	07-02-1990	JP JP JP	1974973 C 2041363 A 7000744 B	27-09-1995 09-02-1990 11-01-1995
Α	27-05-1994	NONE		
Α	13-03-1996	NONE		
	A 	A 09-01-2002 A 07-02-1990 A 27-05-1994	A 09-01-2002 NONE A 07-02-1990 JP JP JP JP A 27-05-1994 NONE	A 09-01-2002 NONE A 07-02-1990 JP 1974973 C JP 2041363 A JP 7000744 B A 27-05-1994 NONE