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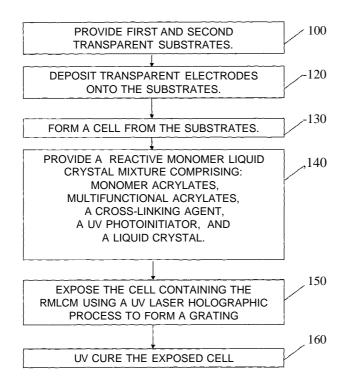


FIG.4

(57) Abstract: There is provided a method of fabricating a HPDLC device comprising the steps of: providing first and second transparent substrates; depositing switchable transparent electrodes elements on each of the first and second transparent substrates; forming a cell from the first and second transparent substrates; providing a reactive monomer liquid crystal mixture comprising a mixture of monomer acrylates, multi-functional acrylates, a cross-linking agent, a UV photoinitiator, a surfactant and a liquid crystal; exposing the cell to first laser wavelength light using a laser holographic recording procedure to form a grating; and exposing the cell to UV curing radiation. In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises a photo-initiator operating in a spectral band including the first laser wavelength. In one embodiment of the invention the first laser wavelength lies in the UV band. In one embodiment of the invention the first laser wavelength lies in the visible band.

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IMPROVEMENTS TO HOLOGRAPHIC POLYMER DISPERSED LIQUID CRYSTAL MATERIALS AND DEVICES

REFERENCE TO PRIORITY APPLICATION

This application claims the priority of United States Provisional Patent Application No. 61/573,066 with filing date 24 August 2011 entitled "Holographic Polymer Dispersed Liquid Crystal Materials and Devices".

REFERENCE TO RELATED APPLICATIONS

Each of the following applications is incorporated herein by reference in its entirety.

PCT Application No.:-US2008/00 1909, with International Filing Date: 22 July 2008, entitled LASER ILLUMINATION DEVICE; PCT Application No.: US2006/04393S, entitled METHOD AND APPARATUS FOR PROVIDING A TRANSPARENT DISPLAY; PCT Application No.: PCT/GB20 10/00 1982 entitled COMPACT EDGE ILLUMINATED EYEGLASS DISPLAY PCT Application No.:PCT/GB20 10/000835 with International Filing Date: 26 April 2010 entitled COMPACT HOLOGRAPHIC EDGE ILLUMINATED EYEGLASS DISPLAY; and PCT Application No.: PCT/GB20 10/002023 filed on 2 November 201 0 entitled APPARATUS FOR REDUCING LASER SPECKLE.

This application incorporates by reference in its entirety the U.S. Patent Application: Ser. No. 10/555,661 filed 4 November 2005 entitled SWITCHABLE VIEWFINDER DISPLAY.

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BACKGROUND OF THE INVENTION

This invention relates to photopolymerizable materials and in particular holographic polymer dispersed liquid crystal materials and processes for fabricating switchable gratings devices.

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There is a requirement for optical switching devices for use in displays, telecommunications optical networks, sensors and other applications. An important class of diffractive optical element known as an electrically Switchable Bragg Gratings (SBG) is based on recording Bragg gratings into a holographic polymer dispersed liquid crystal (HPDLC) mixture. Typically, SBGs are fabricated by first placing a thin film of a mixture of photopolymerizable monomers and liquid crystal material between parallel glass plates. One or both glass plates support electrodes, typically transparent indium tin oxide films, for applying an electric field across the film. A volume phase grating is then recorded by illuminating the liquid material (often referred to as the syrup) with two mutually coherent laser beams, which interfere to form a slanted fringe grating structure. During the recording process, the monomers polymerize and the mixture undergoes a phase separation, creating regions densely populated by liquid crystal micro-droplets, interspersed with regions of clear polymer. The alternating liquid crystal-rich and liquid crystal-depleted regions form the fringe planes of the grating. The resulting volume phase grating can exhibit very high diffraction efficiency, which may be controlled by the magnitude of the electric field applied across the film. When an electric field is applied to the grating via transparent electrodes, the natural orientation of the LC droplets is changed causing the refractive index modulation of the fringes to reduce and the hologram diffraction efficiency to drop to very low levels. Note that the diffraction efficiency of the device can be adjusted, by means of the applied voltage, over a continuous range. The device exhibits

near 100% efficiency with no voltage applied and essentially zero efficiency with a sufficiently high voltage applied. In certain types of HPDLC devices magnetic fields may be used to control the LC orientation. In certain types of HPDLC phase separation of the LC material from the polymer may be accomplished to such a degree that no discernible droplet structure results. U. S. Patent 5,942,157 by Sutherland et al. and U. S Patent 5,751,452 by Tanaka et al. describe monomer and liquid crystal material combinations suitable for fabricating SBG devices.

SBGs may be used to provide transmission or reflection gratings. SBGs may be implemented as waveguide devices in which the HPDLC forms either the waveguide core or an evanescently coupled layer in proximity to the waveguide. In another configuration to be referred to here as Substrate Guided Optics (SGO) the parallel glass plates used to form the HPDLC cell provide a total internal reflection (TIR) light guiding structure. Light is "coupled" out of the SBG when the switchable grating diffracts the light at an angle beyond the TIR condition. SGOs are currently of interest in a range of display and sensor applications. Although much of the earlier work on HPDLC has been directed at reflection holograms transmission devices are proving to be much more versatile as optical system building blocks.

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Typically, recipes for HPDLC comprise liquid crystal (LC), monomers, photoinitiator dyes, and coinitiators. The mixture (often referred to as syrup) frequently includes a surfactant.

The monomers are typically acrylates. Examples of such recipes may-be found in papers dating back to the early 1990s. Acrylates offer the benefits of fast kinetics, good mixing with other materials and compatibility with film forming processes. Since acrylates are cross-linked they tend to be mechanically robust and flexible. For example, urethane acrylates of functionality 2

(di) and 3 (tri) have been used extensively for HOPLC technology. Higher functionality materials such as penta and hex functional stems have also been used. It has been found that the best optical performance typically comes from mixtures of different functionalities. Examples of prior art follow.

a) A paper by R. L. Sutherland et al, Chem. Mater. 5, 1533 (1993) describes the use of acrylate polymers and surfactants. Specifically, the recipe comprises a crosslinking multifunctional acrylate monomer; a chain extender N-vinyl pyrrolidinone, LC E7, photo-initiator rose bengal and coinitiator N-phenyl glycine. Surfactant octanoic acid was added in certain variants.

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b) A paper by Fontecchio et al entitled "Spatially Pixelated Reflective Arrays from Holographic Polymer Dispersed Liquid Crystals", SID 00 Digest 774-776, 2000 describes a UV curable HPDLC for reflective display applications comprising a multi functional acrylate monomer, LC, a photoinitiator a coinitiator and a chain terminator.

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c) United States Patent No.5, 942,157 by Sutherland, et al., issued August 24, 1999 entitled "Switchable volume hologram materials and devices", Application No. 08/680,292 Filed: July 12, 1996 discloses "a new photopolymerizable material allows single-step, fast recording of volume holograms with properties that can be electrically controlled. Polymer-dispersed liquid crystals (PDLCs) in accordance with the invention preferably comprise a homogeneous mixture of a nematic liquid crystal and a multifunctional pentaacrylate monomer, in combination with photoinitiator, coinitiator and cross-linking agent." a surfactant such as octanoic acid may also be added to the above mixture.

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Although the claims are directed at reflection holograms the specification mentions the use of the recipe in transmission holograms (but not edge lit holograms).

- d) The use of acrylates has been reported in several papers. For example a paper entitled "Optimization of Holographic PDLC for Ternary Monomers" by Y.H. Cho, et al (in Polymer International, 48, 1085-1090, 1999) discloses HPDLC recipes including acrylates. A Matsushita Corporation paper by Karasawa et al, entitled "Effects of Material Systems on the Polarization Behavior of Holographic Polymer Dispersed Liquid Crystal Gratings" (in the Japanese Journal of Applied Physics, Vol. 36, 6388-6392, 1997) describes acrylates of various functional orders. A paper by T.J. Bunning et al, entitled "Morphology of Anisotropic Polymer Dispersed Liquid Crystals and the Effect of Monomer Functionality", (Polymer Science: Part B: Polymer Physics, Vol. 35, 2825-2833 1997) describes multifunctional acrylate monomers. A paper by G.S. Iannacchione et al entitled "Deuterium NMR and morphology study of copolymer dispersed liquid crystal Bragg gratings", (Europhysics Letters Vol. 36 (6). 425-430. 1996) describes an HPDLC mixture comprising a penta-acrylate monomer, LC, chain extender, coinitiator and photoinitiator.
- e) The use of surfactants in HPDLC is well known and dates back to the earliest

 investigations of HPDLC. For example, a paper by R.L Sutherland et al, entitled "The physics of photopolymer liquid crystal composite holographic gratings" (presented at SPIE: Diffractive and Holographic Optics Technology San Jose (CA), 1-2 February

 1996, SPIE Vol. 2689, 158-169, 1996) describes an HPDLC mixture comprising a

monomer, photoinitiator, co initiator, chain extender and LC to which a surfactant may be added. Surfactants are also mentioned in a paper by Natarajan et al entitled "Electro Optical Switching Characteristics of Volume Holograms in Polymer Dispersed Liquid Crystals", (Journal of Nonlinear Optical Physics and Materials, Vol. 5 No.1 89-98, 1996).

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f) United States Patent No. 7,018,563 by Sutherland; et al. issued March 28, 2006 entitled "Tailoring material composition for optimization of application specific switchable holograms" (U.S. Patent Application. No.: 10/303,927 filed: November 26, 2002) claims polymer-dispersed liquid crystal material for forming a polymer-dispersed liquid crystal optical element comprising: at least one acrylic acid monomer; at least one type of liquid crystal material; a photoinitiator dye; a co-initiator; and a surfactant. The 563 patent appears to be directed mainly at HPDLC reflection holograms. It is doubtful whether the teachings would apply to transmission holograms. The 563 patent contains no reference to edge lit holograms. The first claim of the 563' patent eliminates the cross-linking monomer recited in prior art such as the Sutherland 157' patent and the Sutherland 1993 paper. However the patent does not teach how to make a HPDLC that avoids the use of a cross-linking monomer (or chain extender). On the contrary, in the specification it is made very clear that in preferred embodiments the recipe includes a chain extender (or cross-linking monomer).

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Prior art in reverse mode SBGs

A fundamental feature of SBGs fabricated using current HPDLC material systems is that the grating is present when the device is in its passive state. An electric field must be applied

across the HPDLC layer to clear the grating. The concept of a reverse mode SBG in which the grating is clear when in its passive state is known but has not been investigated in any great depth. There is little published material on reverse mode transmission gratings.

5 Zhang et al (Syracuse University, Department of Chemistry and W.M. Keck Center for Molecular Electronics, Syracuse, NY) have reported holographically recorded reverse-mode transmission gratings in HPDLC in two published papers (Zhang, J.; Sponsler, M. B. Switchable Liquid Crystalline Photopolymer Media for Holography. J. Am. Chem. Soc. 1992, 114, 1506-1507 and Zhang, J.; Carlen, C. R.; Palmer, S.; Sponsler, M. B. Dynamic Holographic Gratings 10 Recorded by Photopolymerisation of Liquid Crystalline Monomers. J. Am. Chem. Soc. 1994, 116, 7055-7063). An alignment-controlled reverse-mode reflective H-PDLC was been demonstrated by Kato and co-workers in NTT Corporation (Japan) in 1999. (K. Kato, T. Hisaki, and M. Date, Japanese. Journal of Applied Physics. 38, 805 (1999).) The University of Texas has investigated reverse mode transmission SBGs (R.A Ramsey, "Materials for Diffractive 15 Optical Elements", PhD Thesis, University of Texas, December 2006 and R.A. Ramsey and S. C. Sharma Applied Physics B: Laser and Optics Volume 93, Numbers 2-3, 481-489). The SBGs were recorded at 540nm and the recipe comprised a mixture of a reactive mesogenic monomer (mesogen), RM257 (EM Industries), nematic liquid crystals E44 and E3100-100, acrylate monomers(eg trimethylolpropane triacrylate), and a photo-oxidant dye. The reactive 20 mesogen used in this study is a diacrylate, trade name RM257 (EM Industries). **United States** Patent No.: 7,570,405 B1 by Sutherland et al discloses various embodiments directed at optimizing the performance of SBGs. Improvements directed at improving diffraction efficiency (index modulation), polarization sensitivity, haze response time switching voltage, uniformity

and others are disclosed. The most important embodiment covers reverse (inverse) mode operation by controlling certain anisotropic grating parameters. The key claims cover a reverse mode method for switching between first diffraction state (diffraction efficiency close to zero) with no field applied and second diffraction state (maximum diffraction efficiency) where a field is applied. The grating must be orientated such that P-polarised light is restricted to an incidence angle determined by the dielectric modulation tensor. The approach to reverse mode appears to be based on constraining the beam/grating geometry rather than optimizing the HPDLC chemistry and may as a result be too restrictive for applications requiring greater freedom in specifying diffraction angles.

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The need for the present invention

Switchable Bragg Grating (SBG) devices suffer from several problems. The fundamental problem of the grating being present when no field is applied has already been referred to above. This raises power management and safety issues, particularly in applications such as near-eye displays, particular those intended for avionics and other safety-critical applications where a clear display would be desirable in the event of a power failure. The need to combine several SBG devices in layers exacerbates the problem.

In multilayer SBG architectures the weight and thickness of multiple stacked glass substrates can be a concern particular in near eye displays where the design goal is to achieve spectacle like form factors. Plastics are the solution to overcoming the weight and thickness issues. However a "plastic" SBG raises new problems of compatibility with switching electrodes, susceptibility to environmentally stress and compatibility with the HPDLC recording process

which use UV laser recording. Materials such as polycarbonate which are favored for their low birefringence absorb in the UV band.

The recording process used to make SGO SBGs suffers from the problem that the steepangled reference beam will eventually fall upon an interface with an index of refraction
mismatch. This interface leads to a Fresnel reflection of the reference beam causing it to interfere
with the original object beam, and the pre-reflected reference light. Three separate fringe
structures are formed: the primary set by the primary reference beam and the object beam; a
secondary set by the totally-reflected reference beam and the object beam; and a TIR set caused
by the interaction of the totally-reflected reference beam with the primary reference beam. The
above problems are exacerbated by shrinkage, a change in the thickness of a recording layer that
alters the orientation of the fringe structure, causing the reconstruction angle to change.

There is a requirement for a HPDLC material system optimised for high efficiency, low voltage SGO applications.

There is a requirement for HPDLC material system optimised for reverse mode high efficiency, low voltage SGO applications.

There is a further requirement for a reverse mode SBG device and a method of fabricating a reverse mode SBG device.

There is a further requirement for a plastic SBG compatible with the SBG recording process and a method of fabricating a plastic SBG.

There is a yet further requirement for a reverse mode plastic SBG compatible with the SBG recording process and a method of fabricating a plastic SBG.

SUMMARY OF THE INVENTION

It is a first object of the present invention to provide a HPDLC material system optimised for high efficiency, low voltage SGO applications.

It is a further object of the present invention to provide a HPDLC material system

5 optimised for reverse mode high efficiency, low voltage SGO applications.

It is a further object of the present invention to provide a reverse mode SBG device and a method of fabricating a reverse mode SBG device.

It is a further object of the present invention to provide a plastic SBG compatible with the SBG recording process and a method of fabricating a plastic SBG.

It is a yet further object of the present invention to provide a reverse mode plastic SBG compatible with the SBG recording process and a method of fabricating a plastic SBG.

The objects of the invention are achieved in a first embodiment in which there is provided a method of fabricating a HPDLC device comprising the steps of:

a) providing first and second transparent substrates;

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- b) depositing switchable transparent electrodes elements on each of the first and second transparent substrates;
 - c) forming a cell from the first and second transparent plates;
 - d) providing a reactive monomer liquid crystal mixture comprising a mixture of monomer acrylates, multi-functional acrylates, a cross-linking agent, a UV photoinitiator, a surfactant and a liquid crystal;
 - e) exposing the cell to first laser wavelength light using a laser holographic recording procedure to form a grating; and
 - f) exposing the cell to UV curing radiation.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises a photo-initiator operating in a spectral band including the first laser wavelength.

In one embodiment of the invention the first laser wavelength lies in the UV band.

In one embodiment of the invention the first laser wavelength lies in the visible band.

In one embodiment of the invention the laser wavelength lies in the green band.

In one embodiment of the invention the substrates have a refractive index \mathbf{n}_1 , the liquid crystal has a refractive index \mathbf{n}_j when no electric field is applied across the electrodes, and the liquid crystal has a refractive index \mathbf{n}_2 when an electric field is applied across the electrodes, where \mathbf{n}_1 is greater than \mathbf{n}_2 .

In one embodiment of the invention the substrates have a refractive index \mathbf{n}_1 , the liquid crystal has a refractive index \mathbf{n}_2 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index \mathbf{n}_1 when an electric field is applied across the electrodes, where \mathbf{n}_1 is greater than \mathbf{n}_2 .

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In one embodiment of the invention the substrates have a refractive index n_2 , the liquid crystal has a refractive index n_j when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_2 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .

In one embodiment of the invention the substrates have a refractive index n_2 , the liquid crystal has a refractive index n_2 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_i when an electric field is applied across the electrodes, where n_i is greater than n_2 .

In one embodiment of the invention the substrates have a refractive index 1.6, the liquid crystal has a refractive index 1.6 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index 1.5 when an electric field is applied across the electrodes.

5 In one embodiment of the invention the electrodes are applied to opposing surfaces of the substrates.

In one embodiment of the invention the first and second transparent plates are fabricated from plastic.

In one embodiment of the invention the first and second substrates are fabricated from a polycarbonate.

In one embodiment of the invention the surfactant is omitted from the reactive monomer liquid crystal mixture.

In one embodiment of the invention the method of fabricating a HPDLC device further comprises at least one of the steps of: i) pre-heating the reactive monomer liquid crystal mixture in steps prior to cell filling; ii) filling the cell using a multi step vibration procedure to combine the liquid crystal and polymer ingredients and a vacuum fill method; and iii) freezing the cell; and storing the cell in its frozen state. Steps i) to iii) occur between step d) and step e)

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In one embodiment of the invention method of fabricating a HPDLC device further comprises the step of thermally exposing the cell after said step f).

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises nanoclay material.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises carbon nano tube material.

In one embodiment of the invention the transparent electrodes are fabricated from PDOT conductive polymer.

In one embodiment of the invention the transparent electrodes are fabricated from CNT.

In one embodiment of the invention an environmental coating is applied to an external surface of at least one of the substrates.

In one embodiment of the invention a barrier coating is applied to an internal surface of at least one of the substrates.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises high molecular weight fluoromonomer material, the function of the fluoromonomer material being to reduce the evaporation of the liquid crystal and acrylates.

In one embodiment of the invention the HPDLC device is a SBG.

In one embodiment of the invention the HPDLC device is a sub wavelength grating.

In one embodiment of the invention at least one of the electrodes is patterned to provide a multiplicity of selectively switchable electrode elements.

In one embodiment of the invention at least one substrate surface abutting said reactive monomer liquid crystal mixture has a surface relief structure.

In one embodiment of the invention there is provided an switchable grating device comprising: at least one HPDLC layer sandwiched between first and second transparent substrates, a plurality of independently switchable transparent electrodes elements. The HPDLC device is formed in a reactive monomer liquid crystal mixture comprising: monomer acrylates, multi- functional acrylates, a cross-linking agent, a UV photo-initiator, a surfactant and a liquid crystal.

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In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises a photo-initiator operating in a spectral band including the first laser wavelength.

In one embodiment of the invention the first laser wavelength lies in the UV band.

In one embodiment of the invention the first laser wavelength lies in the visible band.

In one embodiment of the invention the laser wavelength lies in the green band.

In one embodiment of the invention the substrates have a refractive index n_1 , the liquid crystal has a refractive index n_1 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_2 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .

In one embodiment of the invention the substrates have a refractive index n_1 , the liquid crystal has a refractive index n_2 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_1 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .

In one embodiment of the invention the substrates have a refractive index n_2 , the liquid crystal has a refractive index n_1 when no electric field is applied across the electrodes, and the

liquid crystal has a refractive index n_2 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .

In one embodiment of the invention the substrates have a refractive index n_2 , the liquid crystal has a refractive index n_2 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_1 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .

In one embodiment of the invention the substrates have a refractive index 1.6, the liquid crystal has a refractive index 1.6 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index 1.5 when an electric field is applied across the electrodes.

In one embodiment of the invention the electrodes are applied to opposing surfaces of the substrates.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises nanoclay material.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises carbon nano tube material.

In one embodiment of the invention the transparent electrodes are fabricated from PDOT conductive polymer.

In one embodiment of the invention the transparent electrodes are fabricated from CNT.

In one embodiment of the invention an environmental coating is applied to an external surface of at least one of the substrates.

In one embodiment of the invention a barrier coating is applied to an internal surface of at least one of the substrates.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises high molecular weight fluoromonomer material, the function of the fluoromonomer material being to reduce the evaporation of the liquid crystal and acrylates.

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In one embodiment of the invention the HPDLC device is a SBG.

In one embodiment of the invention the HPDLC device is a sub wavelength grating.

In one embodiment of the invention at least one of the electrodes is patterned to provide a multiplicity of selectively switchable electrode elements.

In one embodiment of the invention at least one substrate surface abutting said reactive monomer liquid crystal mixture has a surface relief structure.

A more complete understanding of the invention can be obtained by considering the following detailed description in conjunction with the accompanying drawings wherein like index numerals indicate like parts. For purposes of clarity details relating to technical material that is known in the technical fields related to the invention have not been described in detail.

BRIEF DESCRIPTION OF THE DRAWINGS

- FIG. 1 is a schematic side elevation view of a HPDLC device.
- FIG. 2 is a schematic side elevation view of a HPDLC device.
- FIG.3 is a schematic side elevation view of a reverse mode HPDLC device.
- 5 FIG.4 is a flow chart illustrating a method of fabricating a HPDLC device.
 - FIG.5 is a flow chart illustrating a method of fabricating a HPDLC device.
 - FIG.6 is a flow chart illustrating a method of fabricating a HPDLC device.
 - FIG.7 is a flow chart illustrating a method of fabricating a HPDLC device.
 - FIG.8 is a flow chart illustrating a method of fabricating a HPDLC device.
- 10 FIG.9 is a flow chart illustrating a method of fabricating a HPDLC device.
 - FIG.10 is a flow chart illustrating a method of fabricating a HPDLC device.
 - FIG. 11. is a schematic of a first embodiment of a nanoparticle.
 - FIG. 12. is a schematic of a second embodiment of a nanoparticle.
 - FIG. 13. is a schematic of a third embodiment of a nanoparticle.
- 15 FIG. 14. is a schematic of a polymer dispersed liquid crystal material according to the principles of the invention with a droplet domain containing liquid crystal and nanoparticles.
 - FIG. 15. is a schematic of a polymer dispersed liquid crystal material according to the principles of the invention with a planar domain containing liquid crystal and nanoparticles.
 - FIG. 16. is a schematic of a polymer dispersed liquid crystal material according to the principles
- 20 of the invention with a droplet domain containing liquid crystal and nanoclay platelets.
 - FIG. 17. is a schematic of a polymer dispersed liquid crystal material according to the principles of the invention with a planar domain containing liquid crystal and nanoclay platelets.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be further described by way of example only with reference to the accompanying drawings. It will apparent to those skilled in the art that the present invention may be practiced with some or all of the present invention as disclosed in the following description. For the purposes of explaining the invention well-known features of optical technology known to those skilled in the art of optical design and visual displays have been omitted or simplified in order not to obscure the basic principles of the invention. Unless otherwise stated the term "on-axis" in relation to a ray or a beam direction refers to propagation parallel to an axis normal to the surfaces of the optical components described in relation to the invention. In the following description the terms light, ray, beam and direction may be used interchangeably and in association with each other to indicate the direction of propagation of light energy along rectilinear trajectories. Parts of the following description will be presented using terminology commonly employed by those skilled in the art of optical design. It should also be noted that in the following description of the invention repeated usage of the phrase "in one embodiment" does not necessarily refer to the same embodiment.

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FIG. 1 shows a schematic side elevation view of a portion of an HPDLC device according to the principles of the invention. The portion of the device shown in FIG. 1 comprises a first transparent substrate 10, an HPDLC layer comprising UV flood cured region indicated by 20 surrounding at least one independently switchable grating region indicated by 30 and a transparent substrate layer 40. The switchable grating may be a SBG or a sub-wavelength gratings. The HPDLC layer is sandwiched between the substrates. A set of transparent electrodes, which are not shown, is applied to both of the inner surfaces of the substrates.

Typically, the electrodes are configured such that the applied electric field will be perpendicular to the substrates. The electrodes would typically be fabricated from Indium Tin Oxide (ITO). The light guide layer and substrates 10 and 40 together form a light guide. The grating region 30 contains slanted fringes resulting from alternating liquid crystal rich regions and polymer rich (ie liquid crystal depleted) regions. In the OFF state with no electric field applied, the extraordinary axis of the liquid crystals generally aligns normal to the fringes. The grating thus exhibits high refractive index modulation and high diffraction efficiency for P-polarized light. When an electric field is applied to the HPDLC, the grating switches to the ON state wherein the extraordinary axes of the liquid crystal molecules align parallel to the applied field and hence perpendicular to the substrate. Hence in the ON state the grating exhibits lower refractive index modulation and lower diffraction efficiency for both S- and P-polarized light. Thus the grating region no longer diffracts light. Each grating region may be divided into a multiplicity of grating elements such as for example a pixel matrix according to the function of the HPDLC Typically, the electrode on one substrate surface is uniform and continuous, while electrodes on the opposing substrate surface are patterned multiplicity of selectively switchable grating elements such as for example a pixel matrix according to the function of the HPDLC device to.

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Turning now to the schematic side elevation view of FIG.2 we consider the operation of a SGO SBG device based on the embodiment of FIG. lin more detail. It will be seen that the device further comprises, an input lightguide 70, and beam stop 80. The SBG region sandwiched between substrates comprises at least one grating region 30 and flood cured regions 20a, 20b on either side of the SBG grating region. The grating region has a first surface and a second face. A voltage is applied across the grating region by means of a voltage source 41 and circuitry

indicated schematically by 42. For pixilated SBGs the circuitry may comprises an active matrix scheme of the type commonly used in LCDs. The grating is in its diffracting state when the applied voltage is zero and is cleared when a voltage is applied. The input lightguide 70 is optically coupled to the substrates 10 and 40 such the light from the LED undergoes total internal reflection inside the lightguide formed by 10 and 40. External light from other sources generally indicated as 500 propagates through the device and does not interfere with the propagation of light within the lightguide. Turning again to FIG.2, the propagation of light from the source through the device may be understood by considering the state when the SBG is diffracting, that is with no electric field applied. The rays 101 and 102 emanating from the light source 60 are guided initially by the input lightguide 70. The ray 102, which impinges on the second face of the grating region 30, is diffracted out of the device in the direction 201. On the other hand, the rays 101 which do not impinge on the grating region 30 will hit the substrate-air interface at the critical angle and are totally internally reflected in the direction 103 and eventually collected at the beam stop 80. When an electric field is applied to the SBG, the grating switches to the ON state wherein the extraordinary axes of the liquid crystal molecules align parallel to the applied field and hence perpendicular to the substrate. Note that the electric field due to the planar electrodes is perpendicular to the substrate. Hence in the ON state the grating exhibits lower refractive index modulation and lower diffraction efficiency for both S- and P-polarized light. Thus the grating region 12 no longer diffracts light. It should be appreciated that the basic principles of the device illustrated in FIGS. 1-2 may be applied in a wide range of different display, optical telecommunications and sensor applications.

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FIG.3 illustrates a reverse mode grating device similar to the one illustrated in FIG.2. The grating is in its non-diffracting (cleared) state when the applied voltage is zero and switches to its diffracting stated when a voltage V_m is applied across the electrodes.

The inventors have made several inventive steps directed at HPDLC material optimization for SBG optical devices. Firstly, the inventors have developed a new HPDLC. Secondly, the inventors have developed a HPDLC optimized for Substrate Guide Optics (SGO) application. Uniquely, the HPDLC provides an almost complete phase separation of the LC from the polymer for SGO, not only resulting in virtually no-droplet structure, but also higher than 92% diffraction efficiency. This higher efficiency may be used to reduce power consumption or, alternatively, to maximize light throughput.

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The proposed HPDLC formulation is essentially a reactive monomer liquid crystal mixture (RMLCM), which comprises monomer acrylates, multi-functional acrylates, a cross-linking agent, a photo-initiator, a surfactant and a liquid crystal (LC). For the purposes of describing the invention a surfactant is defined as any chemical agent that lowers the surface tension of the total liquid mixture. The earliest references teaching a similar HPDLC have been summarized above. A key feature of the RMLCM is its emphasis on low functionality monomers. The inventors have achieved nearly complete phase separation of the LC material from the polymer resulting in virtually no observable droplet structure. The latter effect has been confirmed by Scanning Electron Microscope (SEM) analysis. The RMLCM yields index modulation of 0.08 to 0.1 1 where the index modulation is given by (ne - no)/2 where ne is the extraordinary refractive index and no is the ordinary refractive index. Higher index

modulations translate to much higher diffraction efficiency (92%) resulting in higher brightness and contrast. In HPDLC developed by other researchers, the index modulation is much smaller. One of the reasons that such levels of performance have been recorded in earlier work may be due to the greater emphasis on reflective HPDLC. Developers of reflective HPDLC would not be motivated to provide a continuous LC layer since a droplet structure is probably necessary in reflective gratings to keep the fringes in place. It is believed that edge-lit transmission mode gratings avoid this problem because the fringes are supported at both ends by the substrates. Desirably the RMLCM cell is enclosed in a thermostat-equipped chamber below room temperature before vacuum sealing since this procedure avoids changes to the formulation.

The basic geometry of edge lit holograms inherently results in total internal reflection (TIR) and secondary fringes during recording. These "spurious gratings" conspire to deplete the principle transmission-mode grating of modulation. To compensate, a RMLCM must provide very high refractive index modulation, especially in high temperature conditions where the LC clear point further reduces index modulation.

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The inventors believe that the RMLCM disclosed in the present application, and the process for which it has been developed may be clearly be differentiated from competitor HPDLC processes. The novel characteristics of the proposed electro-optic nano-composite material and fabrication process are:-

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1. The RMLCM significantly reduces ingredient evaporation during vacuum filling of the RMLCM cell by judicious choice of high molecular weight fluoromonomers and compensation methods. The latter is not obvious or taught by any references known to the inventors. Standard

materials boil off completely within the vacuum fill duty cycles commonly used in existing processes. The inventors were able to tightly control the process and calculate the boil-off amount for several typical cycle times and thereby compensate the particular vacuum fill machine pump-down and fill cycle.

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- 2. Compensation is made for ingredient evaporation during vacuum fill by increasing the concentrations of ingredients subject to evaporation. It is necessary to increase concentration of ingredients beyond the level that is optimal for best device performance.
- 10 3. The RMLCM is preheated in steps prior to cell filling to initiate a cross link of the polymer matrix and improve performance.
 - 4. A multi step vibration procedure is used to combine the LC and polymer ingredients combined with the use of a vacuum fill method to ensure quick filling.

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- 5. The cells are frozen and stored in their frozen state after vacuum filling. Providing frozen pre-exposed blank cells has several benefits in the subsequent exposure process.
- a) Firstly, the LC/Polymer dispersion remains optimal over time. The inventors have discovered that the LC and Monomer separate over time if not kept frozen prior to exposure.
- b) Secondly, any cross-linking chemical monomer reaction is suppressed. The inventors have discovered that if the HPDLC mixture constituents are not frozen before exposure they will tend to react.

c) Thirdly, the critical ingredients susceptible to evaporation at room temperature are suppressed. The inventors have found that a change in material concentrations may occur over time due to evaporation if the RMLCM constituents are not frozen before exposure.

- 5 6. The cells are exposed using a holographic laser exposure procedure.
 - 7. The cells are cured.

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8. The cells are thermally exposed after curing to improve phase separation and hence
 10 diffraction efficiency and prevent any voltage creep by arresting any active ingredients not already completely polymerized.

A method of fabricating a RMLCM in accordance with the basic principles of the invention is shown in FIG.4. Referring to the flow diagram 100, we see that the said method comprises the following steps.

In step 100 first and second transparent substrates are provided.

In step 120 transparent electrodes elements are deposited on each of the first and second transparent substrates.

20 In step 130 a cell is formed from the first and second transparent substrates.

In step 140 a reactive monomer liquid crystal mixture comprising a mixture of monomer acrylates, multi-functional acrylates, a cross-linking agent, a UV photo-initiator, a surfactant and a liquid crystal is provided.

In step 150 the cell containing the RMLCM is exposed to UV wavelength light using a laser holographic recording procedure to form a grating.

In step 160 the cell is exposed to UV curing radiation.

In one embodiment of the invention directed at a reverse mode HPDLC devices the reactive monomer liquid crystal mixture further comprises a photo-initiator operating in a spectral band including the first laser wavelength.

Referring to the flow diagram of FIG. 5 a method of fabricating a reversed mode HPDLC device comprises the following steps:

In step 100 first and second transparent substrates are provided.

In step 120 transparent electrodes elements are deposited on each of the first and second transparent substrates.

In step 130 a cell is formed from the first and second transparent substrates.

In step 141 a reactive monomer liquid crystal mixture comprising a mixture of monomer acrylates, multi-functional acrylates, a cross-linking agent, a UV photo-initiator, a first wavelength photoinitiator, a surfactant and a liquid crystal is provided.

In step 15 1 the cell containing the RMLCM is exposed to first wavelength light using a laser holographic recording procedure to form a grating.

20 In step 160 the cell is exposed to UV curing radiation.

In one embodiment of the invention the first laser wavelength lies in the visible band. In one embodiment of the invention the laser wavelength lies in the green band.

In one embodiment of the invention the substrates have a refractive index n_i , the liquid crystal has a refractive index n_1 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_2 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .

Referring to the flow diagram of FIG.6 a method of fabricating a reversed mode HPDLC device comprises the following steps:

In step 100 first and second transparent substrates are provided.

10 In step 120 transparent electrodes elements are deposited on each of the first and second transparent substrates.

In step 130 a cell is formed from the first and second transparent substrates.

In step 142 a reactive monomer liquid crystal mixture comprising a mixture of monomer acrylates, multi-functional acrylates, a cross-linking agent, a UV photo-initiator, a first wavelength photoinitiator, a surfactant and a liquid crystal having refractive index m_{in} its passive state and refractive index $n_{2} < n_{1}$ when an electric field is applied is provided. In step 151 the cell containing the RMLCM is exposed to first wavelength light using a laser holographic recording procedure to form a grating.

In step 160 the cell is exposed to UV curing radiation.

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Referring to FIG.7 in one embodiment of the invention the RMLCM further compromises a surfactant.

Assuming that the LC is switched between minimum value n_2 and maximum value n_1 and the substrate index is chosen to be either n_i or n_2 the invention as illustrated by the flowcharts of FIGS.4-7 may be used to provide four different configurations which may be summarized as follows:

- A) In one embodiment of the invention the substrates have a refractive index n_1 , the liquid crystal has a refractive index n_1 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_2 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .
- B) In one embodiment of the invention the substrates have a refractive index n₁, the liquid crystal has a refractive index n₂ when no electric field is applied across the electrodes, and the liquid crystal has a refractive index m when an electric field is applied across the electrodes, where n i is greater than n₂.
 - C) In one embodiment of the invention the substrates have a refractive index n_2 , the liquid crystal has a refractive index n_1 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index n_2 when an electric field is applied across the electrodes, where n_1 is greater than n_2 .

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D) In one embodiment of the invention the substrates have a refractive index n_2 , the liquid crystal has a refractive index n_2 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index ni when an electric field is applied across the electrodes, where nj is greater than n_2 .

Typically the lower LC index n₂ is chosen to be as close as possible to the index of the polymer rich regions of the HPDLC. Note that in practice the HPDLC does not simply comprise LC regions separated by polymer regions but rather regions characterised by high concentrations of

LC droplets suspended in polymer separated by regions characterised by relatively low concentrations of LC suspended in polymer. (However, the inventors have found that their material systems are yielding LC-polymer phase separation that conforms well to such a model). Hence the indices n_1 , n_2 may more realistically be defined as the average refractive indices of the high LC concentration and low LC concentration regions respectively.

In one embodiment of the invention the substrates have a refractive index 1.6, the liquid crystal has a refractive index 1.6 when no electric field is applied across the electrodes, and the liquid crystal has a refractive index 1.5 when an electric field is applied across the electrodes.

Referring to the embodiment of FIG.8 in one embodiment of the invention the process of fabricating a HPDLC device further comprises at least one of the following steps.

In step 145 the RMLCM is pre-heated in steps prior to cell filling.

In step 146 the cell is filled using a multi step vibration procedure to combine the liquid crystal and polymer ingredients and a vacuum fill method.

In step 147 the cell is frozen.

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In step 148 the cell is stored in its frozen state.

Steps 145-148 occur between step 140 and 160 in the earlier flow charts.

Referring to the FIG.9 in one embodiment of the invention a method of fabricating a HPDLC device further comprises the step of thermally exposing the cell after said step 160.

In the embodiment of FIG. 10 the substrates are fabricated from polycarbonate. In all other respects the embodiment is identical to the one of FIG. 6 with step 100 being replaced by step 101.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises carbon nano tube (CNT) material.

In one embodiment of the invention the reactive monomer liquid crystal mixture further comprises high molecular weight fluoromonomer material, the function of the fluoromonomer material being to reduce the evaporation of the liquid crystal and acrylates.

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In one embodiment of the invention at least one substrate surface abutting said reactive monomer liquid crystal mixture has a surface relief structure. The surface relief structure may comprise one or two dimensional micro prisms disposed in a regular patter or randomly. The micro prisms may have different sizes. The surface relief structure may comprise at least one waveguide cavity.

In further embodiments of the invention the RMLCM may use LCs incorporating nanoclay nanoparticles within the LC domains. Reductions of switching voltage and improvements to the electro-optic properties of a polymer dispersed liquid crystal film and/or polymer dispersed liquid crystal device may be obtained by including nanoclay nanoparticles in the liquid crystal domains. The inclusion of nanoclay serves to align the liquid crystal molecules and to alter the birefringent properties of the film through index of refraction averaging. In addition, the inclusion of the nanoclay nanoparticles improves the switching response of the

liquid crystal domains. Nanoparticles are composed of nanoclay nanoparticles, preferably spheres or platelets, with particle size on the order of 2-10 nanometers in the shortest dimension and on the order of 10 nanometers in the longest dimension. Desirably, the liquid crystal material is selected to match the liquid crystal ordinary index of refraction with the nanoclay material. Alternatively, the nanoparticles may composed of material having ferroelectric properties, causing the particles to induce a ferroelectric alignment effect on the liquid crystal molecules, thereby enhancing the electro-optic switching properties of the device. In another embodiment of the invention, the nanoparticles are composed of material having ferromagnetic properties, causing the particles to induce a ferromagnetic alignment effect on the liquid crystal molecules, thereby enhancing the electro-optic switching properties of the device. In another embodiment of the invention, the nanoparticles have an induced electric or magnetic field, causing the particles to induce an alignment effect on the liquid crystal molecules, thereby enhancing the electro-optic switching properties of the device.

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Examples of prior art in nanoparticles are reviewed in the following paragraphs.

US 7,046,439 by Kaminsky et. al. entitled "Optical element with nanoparticles" discloses a dispersion of nanoparticles, including nanoclay, within a thermoplastic. The claims are specifically related to the surface features of the resulting thermoplastic film, and are directed at optical morphological structures such as lenses and mirrors. Kaminsky does not teach the combination of nanoclay dispersions and liquid crystals dispersions.

United States Patent No.: 5,847,787 by Fredley et al. entitled "Low driving voltage polymer dispersed liquid crystal display device with conductive nanoparticles" discloses a method of reducing drive voltage by dispersing conductive nanoparticles in the polymer binder. The claims of the Fredley patent are very specific that the nanoparticles are fully contained within the polymer binder, and are not contained within the liquid crystal droplets.

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United States Patent No.: 6,323,989 B1 by Jacobson et al. entitled "Electrophoretic displays using nanoparticles" discloses an electro-optic medium comprising: a suspending fluid in which two types of particles are suspended. The first type of particles are light transmissive and bearing an electric charge. The second type of particles are smaller than the first type of particles and bear an electric charge of opposite polarity. When no electric field is applied to the medium the second type of particles lie on the surfaces of the first type of particles. When an electric field is applied to the medium the second type of particles are removed from the surfaces of the first type of particles and dispersed through the suspending fluid. Hence the material provides two distinct electrically switchable optical characteristics. Since the material disclosed by Jacobson et al is characterised by surface induced interactions between the two types of suspended it is unlikely to apply to material systems based on nanoclays and liquid crystals.

United States Patent No.: 7,068,898 B2 by Buretea et al. entitled "Nanocomposites" discloses composite materials comprising nanostructures such as nanowires, branched nanowires, nanotetrapods, nanocrystals, and nanoparticles). Methods and compositions for making such nanocomposites are also provided, as are articles comprising such composites.

Waveguides and light concentrators comprising nanostructures (not necessarily as part of a nanocomposite) are additional features of the invention. The materials disclosed by Buretea et al are relevant to semiconductor interactions, primarily conduction band and valence band interactions between a nanoparticle (including wires, rods, spheres, etc.) and the surrounding matrix.

United States Patent Publication No.: 2003/0175004A1 by Garito et al. entitled "Optical polymer nanocomposites" discloses A composite material comprising nanoparticles dispersed within a host matrix. Each nanoparticle may include a halogenated outer coating layer that seals the nanoparticle and prevents agglomeration of the nanoparticles within the host matrix. The invention also includes a process of forming the composite material. The composite material may have various applications including, such as optical devices, windowpanes, mirrors, mirror panels, optical lenses, optical lens arrays, optical displays, liquid crystal displays, cathode ray tubes, optical filters, optical components, and others.

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United States Patent Publication No.: 2004/01 56008A1 by Reznikov et al. entitled "Material for liquid crystal cell" discloses a liquid crystal device comprises ferroelectric particles suspended in a liquid crystal material. A method for fabricating a light-modulating device is also disclosed. The method comprises the steps of providing a pair of substrates with a cell gap therebetween, wherein electrodes are disposed on the facing surfaces of the substrates, and permanently disposing a suspension of ferroelectric particles in a liquid crystal material into said cell gap. A method of generating an image comprises providing a pair of substrates with a cell gap therebetween, providing transparent electrodes on each of said substrates adjacent to the cell

gap, permanently disposing a suspension of ferroelectric particles in a liquid crystal material within the cell gap, and applying an electric field across the electrodes.

United States Patent Publication No.: 2004/0225025 A1 by Sullivan et al. "Curable compositions for display devices" discloses curable compositions for the preparation of displays. The compositions are particularly suitable as adhesives, sealants, and/or encapsulants for displays. Compositions according to the invention include those having an epoxy resin and a hydroxy-functional compound, wherein the compositions provide good barrier properties after cure. Sullivan focuses on the sealing properties of the composite, and does not teach how the optical properties or electro-optic properties may be enhanced by the inclusion of nanoclay.

United States Patent Publication No.: 2005/02 18377A1 by Lawandy entitled "Anisotropic nanoparticles and anisotropic nanostrucrures and pixels, displays and inks using them" discloses a pixel that includes a liquid crystal material and one or more of an anisotropic nanoparticle and an anisotropic nanostructure is provided. Displays including the pixel are also disclosed. An ink which includes a liquid crystal material and one or more of an anisotropic nanoparticle and an anisotropic nanostructure is also provided. Lawandy does not teach the use of nanoclay as a nanoparticle, or the effect of nanoparticle doping in liquid crystal or PDLC materials in detail.

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United States Patent Publication No.: 2006/0142455A1 by Agarwal et al. entitled "Polymer compositions, method of manufacture, and articles formed therefrom" discloses a polymer composition, which comprises a matrix polymer, a fluoropolymer that may be at least

partially encapsulated by an encapsulating polymer, and a filler. Methods for making the polymer compositions and articles made of such compositions are also disclosed. The compositions and article can have improved tensile modulus, ductility, and/or impact properties. While this patent claims fluoropolymer encapsulation, the specific claims are related to mechanical properties, and not optical or electro-optical properties. The only discussion of optical properties occurs in the following paragraph, and does not appear to encompass liquid crystal electro-optic films and/or devices.

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In one embodiment of the invention nanoclay nanoparticles are included in the HPDLC material. The inclusion of nanoclay serves to align the liquid crystal molecules and to alter the birefringent properties of the film through index of refraction averaging. One important benefit is a lower switching voltage. In addition, the inclusion of the nanoclay nanoparticles improves the switching response of the liquid crystal domains. The methods for controlling the nanoclay particle size, shape, and uniformity are important to the resulting device properties. In addition, the methods for blending and dispersing the nanoclay particles determine the resulting electrical and optical properties of the device.

FIGS. 11-13 provides schematic illustrations of types of nanoparticles that may be used in the invention. FIG.1 1 is a schematic of a spherical nanoparticle indicated by 1. The diameter of the nanoparticle is less than one micrometer in all three dimensions. Dimension R1 must be less than 0.5 micrometers. This condition results in nanospheres. FIG.12 is a schematic of a nanoparticle indicated by 2. The nanoparticle is characterized by the dimensions R1 and R2 as shown in FIG.12. If R1 is less than R2 and R2 is the radius of a circular cross section the nanoparticle will

be a oblate spheroid. If R1 is greater than R2 and R2 is the radius of a circular cross section the nanoparticle will be a prolate spheroid. The diameter of the nanoparticle is less than one micrometer in at least one dimension. Either R1 or R2 must be less than 0.5 micrometers. This condition results in nanoellipse, nanorod, nanowire, and nanoplatelet configurations. FIG. 13 is a schematic of a nanoparticle indicated by 3. The nanoparticle is a scalene ellipsoid characterized by the dimensions R1, R2 and R3 as shown in FIG. 13. The diameter of the nanoparticle is less than one micrometer in at least one dimension. Either R1 or R2 or R3 must be less than 0.5 micrometers. This condition results in non-uniform configurations, including some types of nanoplatelets and nanosheets. FIG. 14 is a schematic of a polymer dispersed liquid crystal material with a droplet domain containing liquid crystal and nanoparticles. The material as shown in FIG. 14 comprises PDLC droplets such as 11 each containing nano particles such as 31 and liquid crystal regions such as 41. FIG. 15 is a schematic of a polymer dispersed liquid crystal material with a planar domain containing liquid crystal and nanoparticles. The material as shown in FIG. 14 comprises a planar PDLC domain indicated by 12 containing nano particles such as 32 and liquid crystal regions such as 42.

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The invention is not restricted to any particular type of liquid crystal material. The liquid crystal material may be manufactured, refined, or naturally occurring. The liquid crystal material includes all known phases of liquid crystalinity, including the nematic and smectic phases, the cholesteric phase, the lyotropic discotic phase. The liquid crystal may exhibit ferroelectric or antiferroelectric properties and/or behavior.

The invention is not restricted to any particular encapsulating polymer. The encapsulating polymer may be formed from any monomer material that crosslinks and phase

separates when combined in a bi-phase blend with a second material, such as liquid crystal, especially acrylates, thiol-ene, thiol-ester, fluoromonomers, and siloxane based materials. The encapsulating polymer matrix may be a combination of a single monomer or multiple monomer materials. Polymer cross-linking may be achieved through different reaction types, including but not limited to optically-induced photo-polymerization, thermally-induced polymerization, and chemically-induced polymerization.

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The nanoclay nanoparticles may be formed from any naturally occurring or manufactured composition, as long as they can be dispersed in the liquid crystal material. The specific nanoclay material to be selected depends upon the specific application of the film and/or device.

The concentration and method of dispersion also depends on the specific application of the film and/or device.

In the preferred embodiment of the invention, the nanoparticles are composed of

15 nanoclay nanoparticles, preferably spheres or platelets, with particle size on the order of 2-10

nanometers in the shortest dimension and on the order of 10 nanometers in the longest

dimension. Nanoclay is known to have an index of refraction lower than most polymers.

Desirably, the liquid crystal material should be selected to match the liquid crystal ordinary

index of refraction with the nanoclay material. The resulting composite material will have a

20 forced alignment of the liquid crystal molecules due to the nanoclay particle dispersion, and the

optical quality of the film and/or device will be unaffected.

The composite mixture, consisting of the liquid crystal and nanoclay particles, is mixed to an isotropic state by ultrasonication. The mixture can then be combined with an optically crosslinkable monomer, such as acrylated urethane resin that has been photoinitiated, and sandwiched between substrates to form a cell. The preferred substrates are of high optical quality, for example Corning 1737 glass, and coated with a transparent conductive layer, for example indium-tin-oxide ITO). The cell is subsequently exposed to patterned light, and a structured phase separation occurs during photopolymerization, resulting in a holographically formed polymer dispersed liquid crystal (H-PDLC) structure. Said patterned light may be provided by means of conventional laser interference processes using in holographic recording. Alternatively, a masking process may provide said patterned light. Domains of high percentage polymer and domains of high percentage LC/nanoclay are formed in this process. The resulting film/device will have improved electro-optic properties, including diffraction efficiency, extinction ratio, and switching voltage.

Commercially available nanoclay is typically in the form of platelets approximately 1 nanometer thick and 100 nanometers to 10 microns in diameter. The nanoclay may be used in the naturally occurring size distribution, or the particle size may be reduced. The nanoclay may be used with its naturally occurring surface properties, or the surface may be chemically treated for specific binding, electrical, magnetic, or optical properties. Preferably, the nanoclay particles will be intercalcated, so that they disperse uniformly in the liquid crystalline material. The generic term "nanoclay" as used in the discussion of the present invention may refer to naturally occurring montmorillonite nanoclay, intercalcated montmorillonite nanoclay, surface modified motmorillonite nanoclay, and surface treated montmorillonite nanoclay.

The nanoparticles may be useable as commercially purchased, or they may need to be reduced in size or altered in morphology. The processes that may be used include chemical particle size reduction, particle growth, grinding of wet or dry particles, milling of large particles or stock, vibrational milling of large particles or stock, ball milling of particles or stock, centrifugal ball milling of particles or stock, and vibrational ball milling of particles or stock. All of these techniques may be performed either dry or with a liquid suspension. The liquid suspension may be a buffer, a solvent, an inert liquid, or a liquid crystal material. One exemplary ball milling process provided by Spex LLC (Metuchen, NJ) is known as the Spex 8000 High Energy Ball Mill. Another exemplary process, provided by Retsch (France), uses a planetary ball mill to reduce micron size particles to nanoscaie particles.

The nanoparticles need to be dispersed in the liquid crystal material prior to polymer dispersion. Dry nanoparticles may be ultrasonically mixed with the liquid crystal material prior to polymer dispersion to achieve an isotropic dispersion. Wet particles may need to be prepared for dispersion in liquid crystal, depending on the specific materials used. If the particles are in a solvent or liquid buffer, the solution may be dried, and the dry particles dispersed in the liquid crystal as described above. Drying methods include evaporation in air, vacuum evaporation, and heating the solution. If the particles are dispersed in a solvent or liquid buffer with a vapor *pressure* lower than the liquid crystal material, the solution may be mixed directly with the liquid crystal, and the solvent can be evaporated using one of the above methods leaving behind the liquid crystal / nanoparticle dispersion.

In one embodiment of the invention, the optical film comprises a liquid crystal material and a nanoclay nanoparticle, where a nanoparticle is a particle of material with size less than one micrometer in at least one dimension. The film may be isotropically distributed.

In one embodiment of the invention, the optical film comprises a liquid crystal material and a nanoclay nanoparticle, where a nanoparticle is a particle of material with size less than one micrometer in at least one dimension. The film may be stratified into layers.

In one embodiment of the invention, the optical film comprises a liquid crystal material and a nanoclay nanoparticle, where a nanoparticle is a particle of material with size less than one micrometer in at least one dimension. The film may contain domains, of any size, containing the liquid crystal and nanoparticle mixture. The domains may be droplets, planes, or complex lattice structures.

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- 15 FIG. 16 is a schematic of a polymer dispersed liquid crystal material with a droplet domain containing liquid crystal and nanoclay platelets. The material as shown in FIG. 16 comprises PDLC droplets such as 13 each containing nanoclay platelets such as 33 and liquid crystal regions such as 43.
- FIG. 17 is a schematic of a polymer dispersed liquid crystal material with a planar domain containing liquid crystal and nanoclay platelets. The material as shown in FIG. 17 comprises a planar PDLC domain indicated by 14 containing nanoclay platelets such as 34 and liquid crystal regions such as 44.

In another embodiment of the invention, the nanoparticles are composed of material having ferroelectric properties, causing the particles to induce a ferroelectric alignment effect on the liquid crystal molecules, thereby enhancing the electro-optic switching properties of the device.

In another embodiment of the invention, the nanoparticles are composed of material having ferromagnetic properties, causing the particles to induce a ferromagnetic alignment effect on the liquid crystal molecules, thereby enhancing the electro-optic switching properties of the device.

In another embodiment of the invention, the nanoparticles have an induced electric or magnetic field, causing the particles to induce an alignment effect on the liquid crystal molecules, thereby enhancing the electro-optic switching properties of the device.

Embodiments based on Plastic SwitchabLe Bragg Grating Devices

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Plastic substrates offer the benefits of light weight flexibility and thin form factors. The challenges are matching the optical performance of glass substrates, finding conductive material for controlling the ON/OFF state of a plastic SBG and finding a suitable environmental coating to seal the plastic substrates against moisture, harmful organic solvents, and environmental contaminants. Two currently available plastic substrates materials are a cyclic olefin copolymer (COC) manufactured by TOPAS Advanced Polymers and sold under the trade name TOPAS. The other was a cyclic olefin polymer (COP) manufactured by ZEON Corporation and sold under the trade names ZEONEX and ZEONOR. These materials combine excellent optical properties (including high transmission and low birefringence) with excellent physical properties

(including low specific gravity, low moisture absorption, and relatively high glass transition temperature).

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Polymerization kinetics are affected in fundamental ways by the switch from glass to plastic. Two key parameters that directly impact the recording process are the recording temperature and the UV exposure. The inventors have found that high quality gratings can be produced at room temperature and that modest variations in temperature (±10°C) do not affect the quality of the grating. The inventors have also found that the optimal laser exposure for the plastic cells is the same as for the glass cells. This can be explained by the relatively high transparency (>85%) of both TOPAS and ZEONEX at the UV recording wavelength of 365nm. The inventors have found that an adequate DE (i.e. >70%) can be obtained when using plastic substrates. The DE compares favorably with glass. The switching time of plastic SBG is also found to be sufficient to produce satisfactory devices.

Transparent conductive (ITO) coatings applied to the above plastics have been found to be entirely satisfactory, where satisfactory is defined in terms of resistivity, surface quality, and adhesion. Resistivity values were excellent, typically around IOOΩ/square. Surface quality (i.e., the size, number and distribution of defects) was also excellent. Observable defects are typically smaller than lmicron in size, relatively few in number, and sparsely distributed. Such imperfections are known to have no impact on overall cell performance. ITO suffers from the problem of its lack of flexibility. Given the rugged conditions under some SBG devices may operate, it is desirable to use a flexible TCC with a plastic substrate. In addition, the growing cost of indium and the expense of the associated deposition process also raise concerns. Carbon

nanotubes (CNTs), a relatively new transparent conductive coating, are one possible alternative to ITO. If deposited properly, CNTs are both robust and flexible. Plus, they can be applied much faster than ITO coatings, are easier to ablate without damaging the underlying plastic, and exhibit excellent adhesion. At a resistivity of 200D/sq, the ITO coatings on TOPAS 5013S exhibited more than 90% transmission. At a resistivity of 230Q/sq, the CNT coatings deposited on the same substrates material exhibited more than 85% transmission. It is anticipated that better performance wilt results from improvements to the quality and processing of the CNTs. The goal will be to decrease the thickness (to improve transmission) while increasing the conductivity (to keep the resistivity low). One or more of the conductive transparent coatings being developed for flexible displays and photovoltaic applications may be relevant to SBGs.

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An adhesion layer is required to support the transparent conductive coating. The inventors have found that the adhesion of ITO or CNT directly to plastics such as TOPAS and ZEONEX was poor to marginal. The inventors have found that this problem can be overcome by means of a suitable adhesion layer. One exemplary adhesion layer is Hermetic TEC 2000 Hard Coat from the Noxtat Company. This material has been found to yield a clear, mar-resistant film when applied to a suitably prepared plastic substrate. It can be applied by flow, dip, spin, or spray coating. TEC 2000 Hard Coat is designed to give good adhesion to many thermoplastic substrates that are cast, extruded, molded or blow molded. When applied to TOPAS, ZEONEX or other compatible plastics, the strength and break resistance provided by TEC 2000 is nearly as scratch and abrasion resistant as glass. Hermetic Hard Coat forms a transparent 3-6 micron film on plastic surfaces. The Refractive index of the coating is 1.4902. A sample of TOPAS plastic sheet coated with TEC 2000 Noxtat protective Hard Coat is shown in Figure 13. The next step in

SBG cell production process is applying the TCC (ITO or CNT) to the hard coat. Figure 14 shows Noxtat Hard Coat samples with additional ITO and CNT coatings. The Hard Coat plays two roles in SBG cell production. One is to increase adhesion of the conductive layer to the plastic and prevent degasing during vacuum coating. The second role is to seal the plastic surface from environmental influence. It was found that TEC 2000 Hard Coat performs very well with TOPAS and ZEONEX materials.

In one embodiment of the invention an environmental coating is applied to an external surface of at least one of the substrates. The inventors have found that TEC 2000 hard coat works very well as an environmental seal of the SBG cell and as a primer for better adhesion of the conductive coatings such as ITO and CNT. It has also been demonstrated that double side coated TEC 2000 TOPAS and ZEONEX SBG cells perform very well optically and are environmentally stable.

In one embodiment of the invention the first and second substrates are fabricated from a polycarbonate. Polycarbonate is favored for its low birefringence.

In one embodiment of the invention the transparent electrodes are fabricated from PDOT conductive polymer. This material has the advantage of being capable of being spin-coated onto plastics. Typically a PDOT conductive polymer can achieve a resistivity 1000hm/sq.

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In one embodiment of the invention the transparent electrodes are fabricated from CNT.

In one embodiment of the invention at least one substrate surface abutting said reactive monomer liquid crystal mixture has a surface relief structure. The surface relief structure may comprise

one or two dimensional micro prisms disposed in a regular patter or randomly. The micro prism may have different sizes. The surface relief structure may comprise at least one waveguide cavity. In one embodiment of the invention CNT is used to form a printed microstructure using a lift-off stamping process. An exemplary CNT material is the one provided by OpTIC (Glyndwr Innovations Ltd.) St. Asaph, Wales, United Kingdom.

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In one embodiment of the invention CNT is used as an alternative to nanoclay as a means for reducing voltage. The properties of CNT in relation to HPDLC devices are reviewed in a paper entitled "Enhancement of electro-optical properties in holographic polymer-dispersed liquid crystal films by incorporation of multi-walled carbon nanotubes into a polyurethane acrylate matrix" by E.H. Kim et al in Polym Int 2010; 59: 1289-1295 also Published online in Wiley Interscience: 16 June 2010 (www.interscience.wiley.com). Holographic polymerdispersed liquid crystal (HPDLC) films have been fabricated with varying amounts of multiwalled carbon nanotubes (MWCNTs) to optimize the electro-optical performance of the HPDLC films. The MWCNTs were well dispersed in the prepolymer mixture up to 0.5 wt%, implying that polyurethane acrylate (PUA) oligomer chains wrap the MWCNTs along their length, resulting in high diffraction efficiency and good phase separation. The hardness and elastic modulus of the polymer matrix were enhanced with increasing amounts of MWCNTs because of the reinforcement effect of the MWCNTs with intrinsically good mechanical properties. The increased elasticity of the PUA matrix and the immiscibility between the matrix and the liquid crystals (LCs) gradually increased the diffraction efficiency of the HPDLC films. However, the diffraction efficiency of HPDLC films with more than 0.05 wt% MWCNTs was reduced, caused by poor phase separation between the matrix and LCs because of the high viscosity of the

reactive mixture. HPDLC films showing a low driving voltage ($<3~V~\mu\eta\iota$ -l), a fast response time (<10~ms) and a high diffraction efficiency (>75%) could be obtained with 0.05 wt% MWCNTs at 40 wt% LCs.

Although the invention has been discussed in relation to SGO SBG devices the HPDLC

5 material system and fabrication process described herein may also be applied to any type of
HPDLC grating device including SBGs and subwavelength gratings. The devices may be
transmissive or reflective and be used with guided beams or in free-space applications. The
invention may be used to provide more efficient waveguide devices. Such waveguide devices
may be used in Optical Add Drop Multiplexers, Variable Optical Attenuators and many other

10 applications.

The basic invention is not restricted to any particular application and may be used to provide switchable grating devices in any of switchable grating devices disclosed in the following filings which are incorporated by reference herein in their entireties:

- A) PCT Application No.: US2006/043938, claiming priority to US provisional patent application 60/789,595 filed on 6 April 2006, entitled METHOD AND APPARATUS FOR PROVIDING A TRANSPARENT DISPLAY.
- B) U.S. Patent Application: Ser. No. 10/555,661 filed 4 November 2005 entitled SWITCHABLE VIEWFINDER DISPLAY.

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C) PCT Application No.:US2008/001909, with International Filing Date: 22 July 2008,
 20 entitled LASER ILLUMINATION DEVICE. and PCT Application No.:
 PCT/GB20 10/002023 filed on 2 November 2010 by the present inventors entitled
 APPARATUS FOR REDUCING LASER SPECKLE.

D) PCT Application No.: PCT/GB20 10/001982 entitled COMPACT EDGE ILLUMINATED EYEGLASS DISPLAY by the present.

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- E) United States Provisional Patent Application No.61/344,748 with filing date 28

 September 2010 entitled EYE TRACKED HOLOGRAPHIC EDGE ILLUMINATED EYEGLASS DISPLAY).
- F) United States Provisional Patent Application No.61/457,835 with filing date 16 June 2011 entitled HOLOGRAPHIC BEAM STEERING DEVICE FOR AUTOSTEREOSCOPIC DISPLAYS.
- G) PCT Application No.: PCT/GB2010/000835 with International Filing Date: 26 April
 2010 entitled COMPACT HOLOGRAPHIC EDGE ILLUMINATED EYEGLASS
 DISPLAY micro.

It should be understood by those skilled in the art that while the present invention has been described with reference to exemplary embodiments, it is to be understood that the invention is not limited to the disclosed exemplary embodiments. Various modifications, combinations, sub-combinations and alterations may occur depending on design requirements and other factors insofar as they are within the scope of the appended claims or the equivalents thereof.

CLAIMS

What is claimed is:

- 5 1. A method of fabricating a HPDLC device including the steps of:
 - a) providing first and second transparent substrates;
 - b) depositing switchable transparent electrodes elements on each of said first and second transparent substrates;
 - c) forming a cell from said first and second transparent plates;
- d) providing a reactive monomer liquid crystal mixture comprising a mixture of monomer acrylates, multi-functional acrylates, a cross-linking agent, a UV photo-initiator, a surfactant and a liquid crystal;
 - e) exposing said cell to first laser wavelength light using a laser holographic recording procedure to form a grating; and
- f) exposing said cell to UV curing radiation.
 - The method of claim 1 wherein said reactive monomer liquid crystal mixture further comprises a photo-initiator operating in a spectral band including said first laser wavelength.

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3. The method of claim 1 wherein said substrates have a refractive index ni said liquid crystal has a refractive index ni when no electric field is applied across said electrodes,

and said liquid crystal has a refractive index n_2 when an electric field is applied across said electrodes, where n_1 is greater than n_2 .

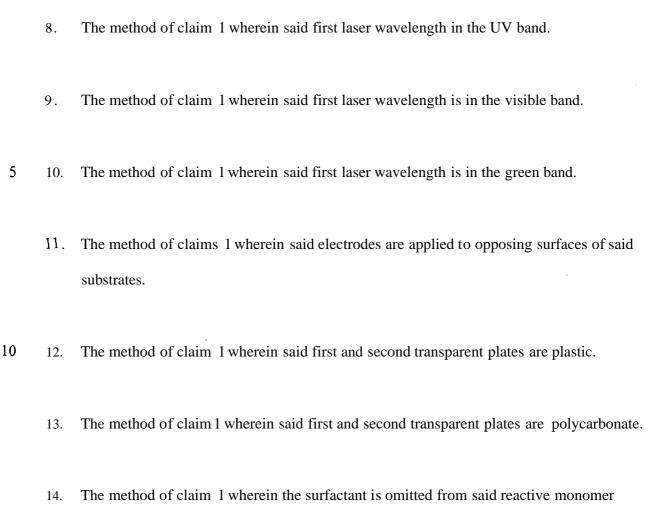
4. The method of claim 1 wherein said substrates have a refractive index ni said liquid crystal has a refractive index n_2 when no electric field is applied across said electrodes, and said liquid crystal has a refractive index ni when an electric field is applied across said electrodes, where n_i is greater than n_2 .

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- 5. The method of claim 1 wherein said substrates have a refractive index n₂ said liquid crystal has a refractive index n₁ when no electric field is applied across said electrodes, and said liquid crystal has a refractive index n₂ when an electric field is applied across said electrodes, where n₁ is greater than n₂.
 - 6. The method of claim 1 wherein said substrates have a refractive index n_2 said liquid crystal has a refractive index n_2 when no electric field is applied across said electrodes, and said liquid crystal has a refractive index ni when an electric field is applied across said electrodes, where n_1 is greater than n_2 .
- 7. The method of claim 1 wherein said substrates have a refractive index 1.6 said liquid

 crystal has a refractive index 1.6 when no electric field is applied across said electrodes, said liquid crystal has a refractive index 1.5 when an electric field is applied across said electrodes.



15. The method of claim 1 further comprising at least one of the steps of:

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liquid crystal mixture.

- i) pre-heating the reactive monomer liquid crystal mixture in steps prior to cell filling;
- ii) filling the cell using a multi step vibration procedure to combine the liquid crystal and polymer ingredients and a vacuum fill method;
 - iii) freezing the cell; and storing the cell in its frozen state, said steps i) to iii) occurring between said steps d) and step e)

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- 16. The method claim 1 further comprising the step of thermally exposing the cell after said step f).
- 17. The method of claim 1 wherein said reactive monomer liquid crystal mixture further comprises nanoclay material.
 - 18. The method of claim 1 said reactive monomer liquid crystal mixture further comprises carbon nano tube material
- 19. The method of claim 1wherein said transparent electrodes are fabricated from PDOT conductive polymer.
 - 20. The method of claim 1wherein said transparent electrodes are fabricated from CNT.
- 15 21. The method of claim 1 wherein an environmental coating is applied to an external surface of at least one of said substrates.
 - 22. The method of claim 1 wherein an adhesive layer is applied between said electrodes and said substrates.
 - 23. The method of claim 1 wherein said reactive monomer liquid crystal mixture further comprises high molecular weight fluoromonomer material, wherein said fluoromonomer material reduces the evaporation of said liquid crystal and said acrylates.

- 24. The method of claim 1 wherein said HPDLC device is a SBG.
- 25. The method of claim 1 wherein said HPDLC is a sub wavelength grating.
- 5 26. The method of claim 1 wherein at least one of said of said electrodes is patterned to provide a multiplicity of selectively switchable electrode elements.
 - 27. The method of claim 1 wherein at least one substrate surface abutting said reactive monomer liquid crystal mixture has a surface relief structure.
 - 28. The method of claim 1 wherein said first and second substrates provide a lightguide.
 - 29. A switchable grating device comprising: at least one HPDLC layer;

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wherein said HPDLC is sandwiched between first and second transparent substrates,
a plurality of independently switchable transparent electrodes elements,
wherein said HPDLC is formed in a reactive monomer liquid crystal mixture,
wherein said reactive monomer liquid crystal mixture comprises monomer acrylates,
multi-functional acrylates, a cross-linking agent, a UV photo-initiator, a surfactant and a
liquid crystal.

30. The apparatus of claim 33 wherein said reactive monomer liquid crystal mixture further comprises a photo-initiator operating in a spectral band including said first laser wavelength.

- The method of claim 33 wherein said substrates have a refractive index n_1 said liquid crystal has a refractive index n_1 when no electric field is applied across said electrodes, and said liquid crystal has a refractive index n_2 when an electric field is applied across said electrodes, where n_1 is greater than n_2 .
- 10 32. The method of claim 33 wherein said substrates have a refractive index n_1 said liquid crystal has a refractive index n_2 when no electric field is applied across said electrodes, and said liquid crystal has a refractive index n_1 when an electric field is applied across said electrodes, where n_1 is greater than n_2 .
- 15 33. The method of claim 33 wherein said substrates have a refractive index n_2 said liquid crystal has a refractive index n_1 when no electric field is applied across said electrodes, and said liquid crystal has a refractive index n_2 when an electric field is applied across said electrodes, where rii is greater than n_2 .
- 20 34. The method of claim 33 wherein said substrates have a refractive index n_2 said liquid crystal has a refractive index n_2 when no electric field is applied across said electrodes, and said liquid crystal has a refractive index ni when an electric field is applied across said electrodes, where n_1 is greater than n_2 .

35. The apparatus of claim 33 wherein said substrates have a refractive index 1.6 said liquid crystal has a refractive index 1.6 when no electric field is applied across said electrodes, said liquid crystal has a refractive index 1.5 when an electric field is applied across said electrodes.

- 36. The apparatus of claims 33 wherein said electrodes are applied to opposing surfaces of said substrates.
- 10 37. The apparatus of claim 33 wherein said first laser wavelength in the UV band.

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- 38. The apparatus of claim 33 wherein said first laser wavelength is in the visible band.
- 39. The apparatus of claim 33 wherein said first laser wavelength is in the green band.
- 40. The apparatus of claim 33 wherein said first and second transparent plates are fabricated from plastic.
- 41. The apparatus of claim 33 wherein said first and second transparent plates are fabricatedfrom polycarbonate.
 - 42. The apparatus of claim 33 wherein the surfactant is omitted from said reactive monomer liquid crystal mixture.

43. The apparatus of claim 33 wherein said first and second substrates provide a lightguide.

44. The apparatus of claim 33 wherein said transparent electrodes are fabricated from PDOT conductive polymer.

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- 45. The apparatus of claim 33 wherein said transparent electrodes are fabricated from CNT.
- 46. The apparatus of claim 33 wherein an environmental coating is applied to an external surface of at least one of said substrates.

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- 47. The apparatus of claim 33 wherein an adhesive layer is applied between said electrodes and substrates.
- 48. The apparatus of claim 33 wherein said reactive monomer liquid crystal mixture further comprises high molecular weight fluoromonomer material, wherein said fluoromonomer material reduces the evaporation of said liquid crystal and said acrylates.
 - 49. The apparatus of claim 33 wherein said HPDLC device is a SBG.
- 20 50. The apparatus of claim 33 wherein said HPDLC is a sub wavelength grating.
 - 51. The apparatus of claim 33 wherein at least one of said of said electrodes is patterned to provide a multiplicity of selectively switchable electrode elements.

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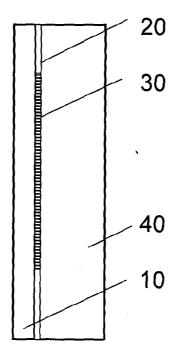
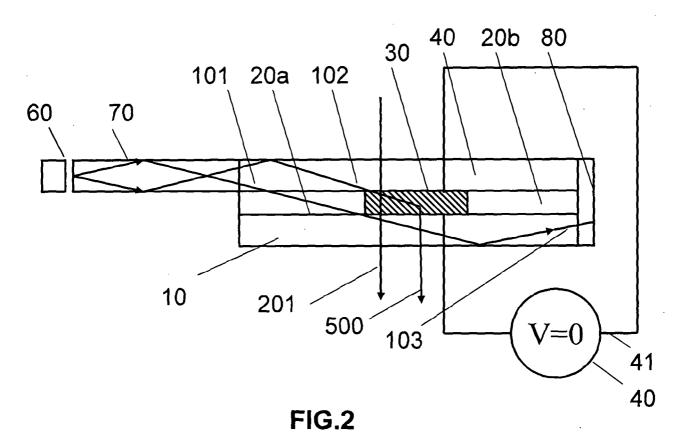
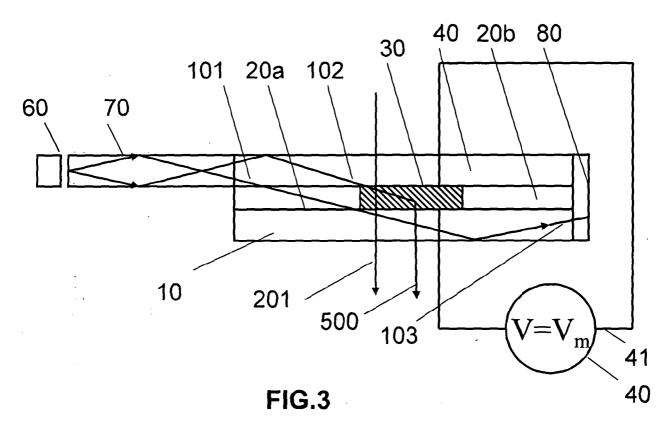


FIG.1





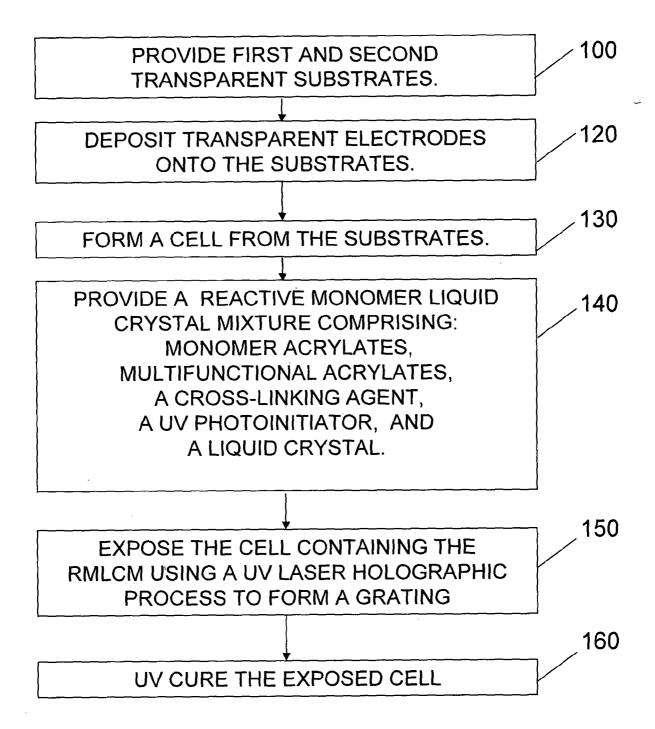


FIG.4

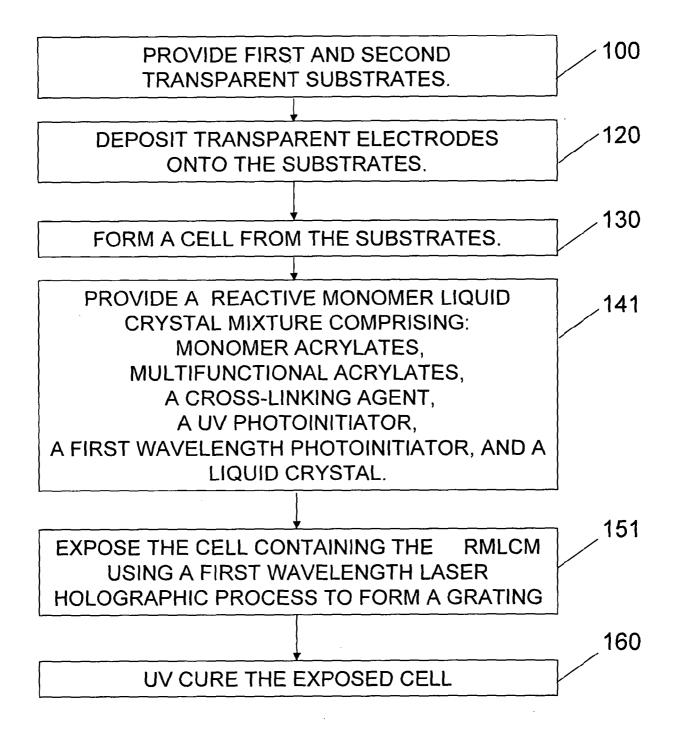


FIG.5

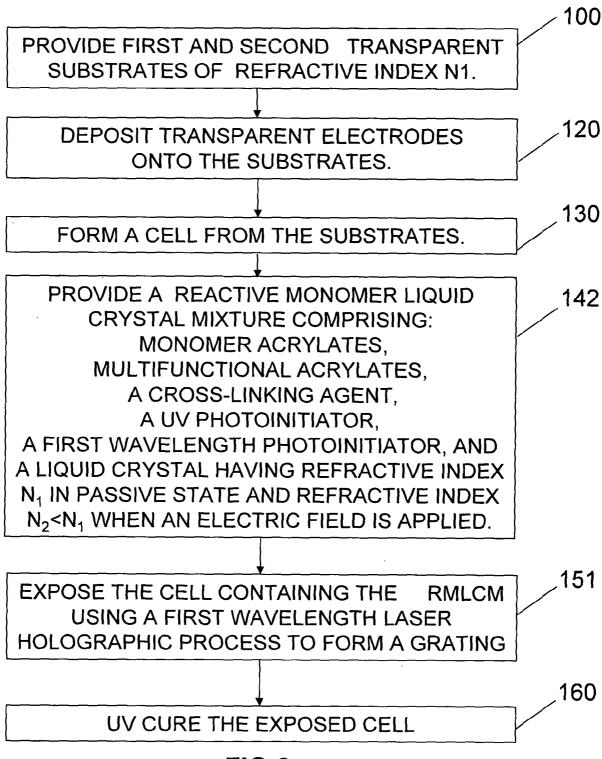


FIG.6

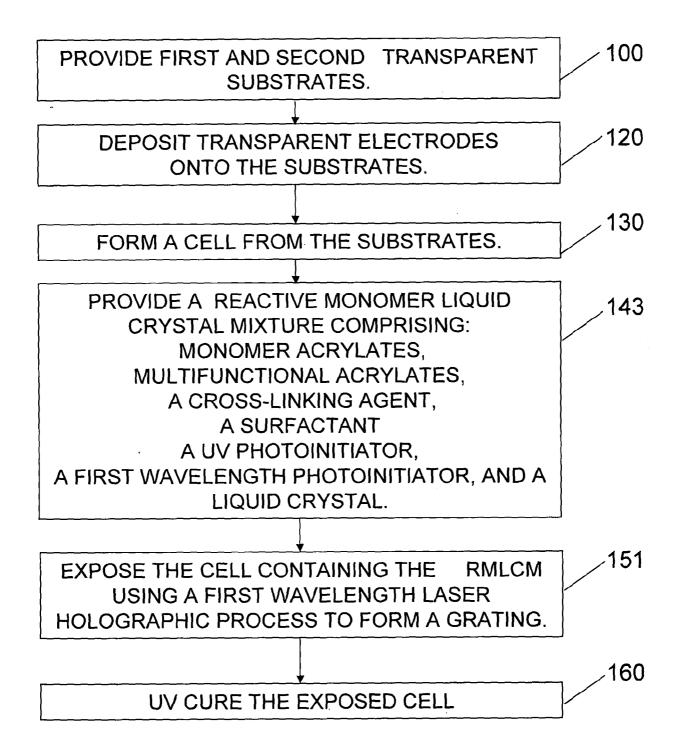


FIG.7

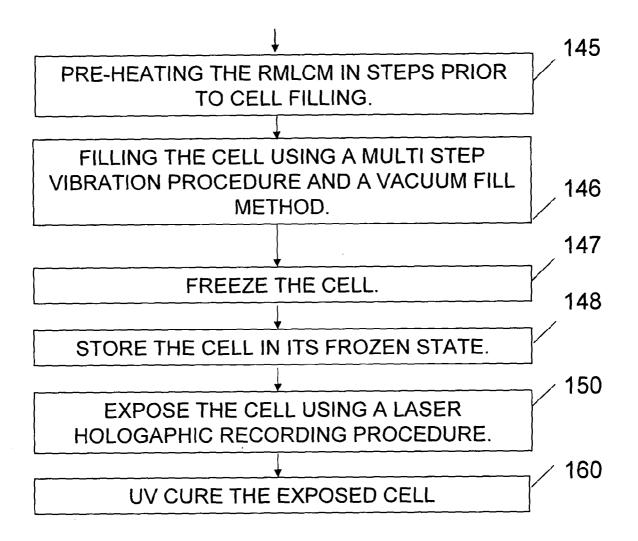


FIG.8

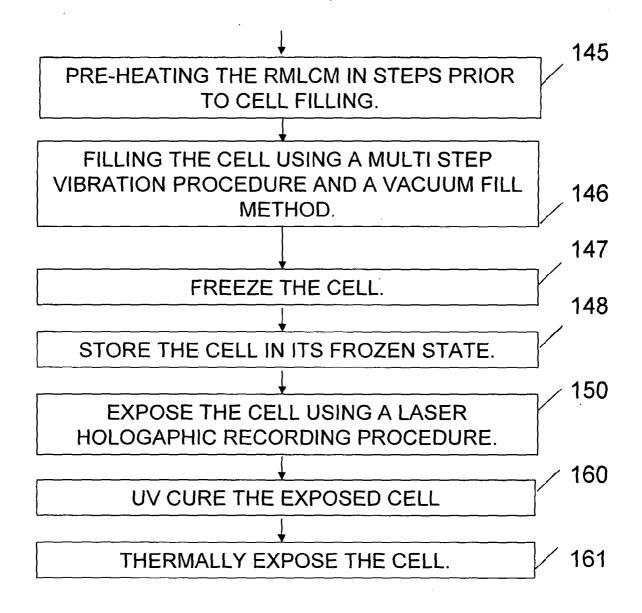


FIG.9

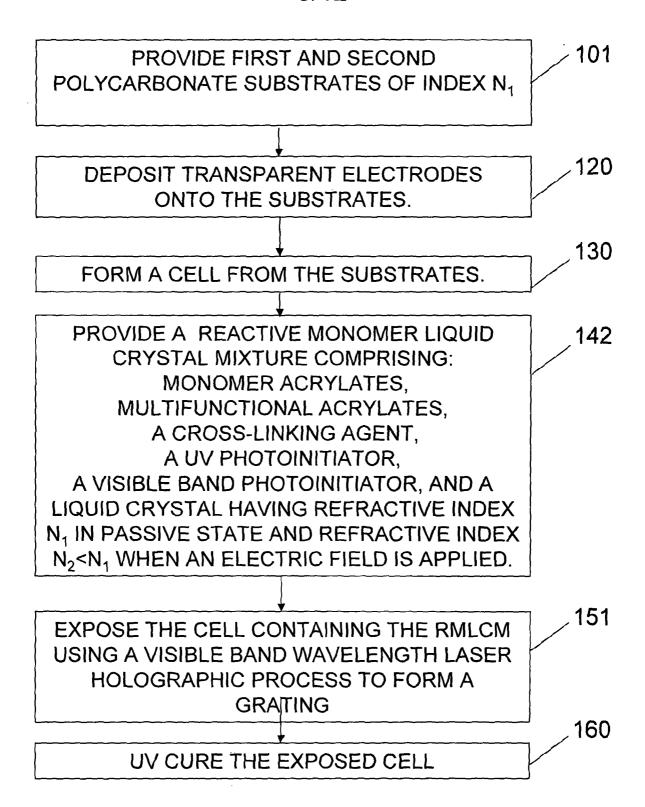
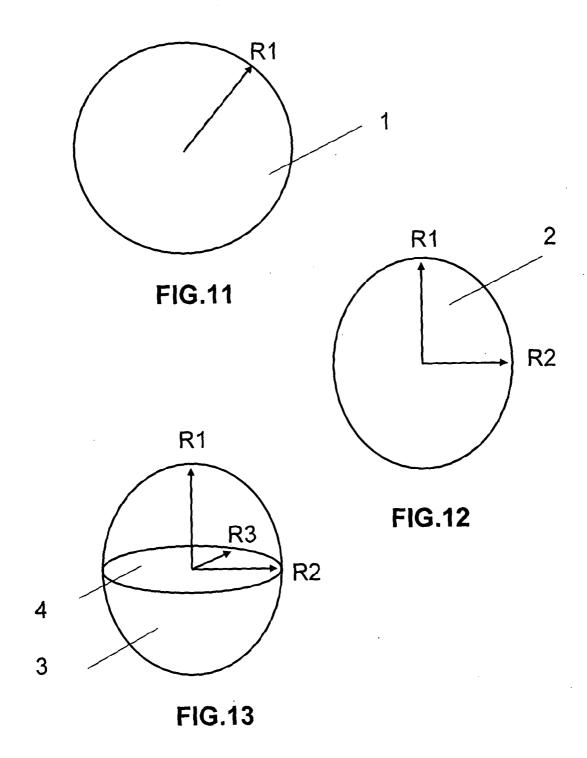


FIG.10





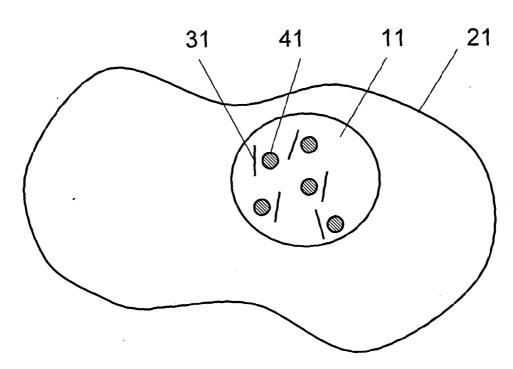


FIG.14

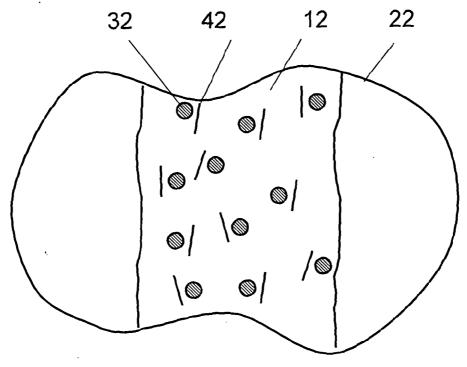


FIG.15

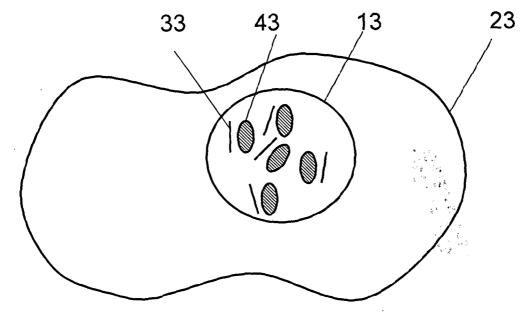


FIG.16

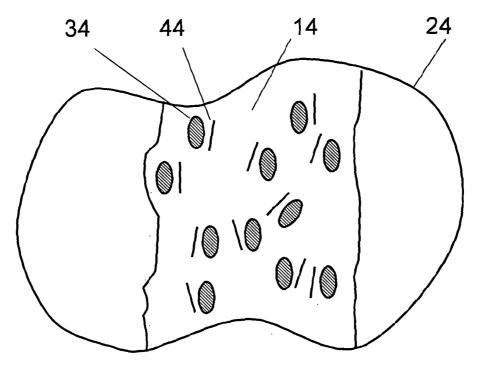


FIG.17

INTERNATIONAL SEARCH REPORT

International application No PCT/GB2012/000680

A. CLASSIFICATION OF SUBJECT MATTER

INV. G02F1/1334

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) ${\tt G02F}$

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

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

EPO-Internal , WPI Data, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Х	US 7 077 984 B1 (NATARAJAN LALGUDI V [US] ET AL) 18 July 2006 (2006-07-18) abstract	1-29
X	US 2006/119916 Al (SUTHERLAND RICHARD L [US] ET AL) 8 June 2006 (2006-06-08) claims 38-43	1,29
X	US 2008/089073 Al (HIKMET RIFAT A M [NL]) 17 April 2008 (2008-04-17) paragraphs [0014] - [0015] paragraph [0073] - paragraph [0078]	1-29

Further documen	ts are listed in the	continuation of Box ${\sf C}$.

Χ

See patent family annex.

- * Special categories of cited documents :
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" documentwhich may throw doubts on priority claim(s) orwhich is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 October 2012	06/11/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Gill, Richard

International application No. PCT/GB2012/000680

INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. X Claims Nos.: 30_51 because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically: See FURTHER INFORMATION sheet PCT/ISA/210
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee. The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuati on of Box 11.2

Cl aims Nos .: 30-51

Claim 33 is drafted as being dependent on claim 33, which is not possible/meaningful. Claims 30-32,34-51 are drafted as being dependent on claim 33, which is not possible because claim 33 itself is not meaningful (see above). In addition claims 30,35-51 are drafted as apparatus claims being dependent on method claim 33, which is not possible due to mixed category of claims.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2012/000680

		date	Patent family member(s)		Publication date	
US 7077984	в1	18-07-2006	NONE]		
US 2006119916	Al	08-06-2006	NONE]		
us 2008089073	Al	17-04-2008	CN EP JP US W 0	101065713 1817643 2008522208 2008089073 2006056937	Al A Al	31-10-2007 15-08-2007 26-06-2008 17-04-2008 01-06-2006