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(71) Applicants (for all designated States except US): **CAMBRIDGE ENTERPRISE LIMITED** [GB/GB]; The Old Schools, Trinity Lane, Cambridge CB2 1TN (GB). **DEUTSCHES KUNSTSTOFF-INSTITUT** [DE/DE]; Schlossgartenstr. 6, Darmstadt 64289 (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BAUMBERG, Jeremy John** [GB/GB]; Department of Physics, Cavendish Laboratory, JJ Thomson Avenue, Cambridge CB3 0HE (GB). **SNOSWELL, David Robert Evan** [GB/GB]; 29 Northfield, Girton, Cambridge CB3 0QG (GB). **BELL, Nicholas Andrew William** [GB/GB]; Jesus College, Cambridge CB5 8BL (GB). **HELLMANN, Gotz Peter**

[DE/DE]; Deutsches Kunststoff-Institut, Schlossgartenstr. 6, 64289 Darmstadt (DE). **SPAHN, Peter Wolfgang Andreas** [DE/DE]; Deutsches Kunststoff-Institut, Schlossgartenstr. 6, 64289 Darmstadt (DE).

(74) Agents: **NAYLOR, Matthew** et al.; Mewburn Ellis LLP, 33 Gutter Lane, London EC2V 8AS (GB).

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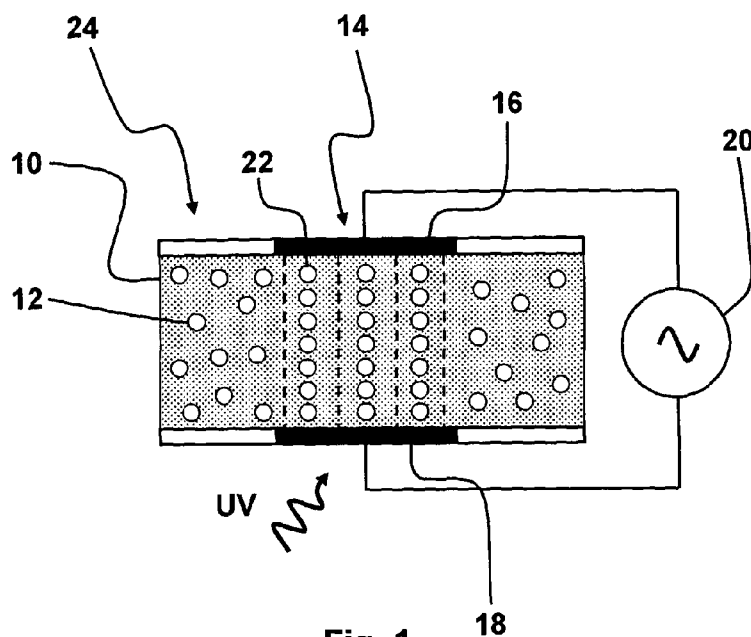


Fig. 1

(57) Abstract: A composite material has a periodic arrangement of particles distributed in a matrix. The refractive index of the material of the particles is different to the refractive index of the material of the matrix and the periodicity is such that, when illuminated with white light, the periodic arrangement provides structural colour. A method of manufacturing the material includes the steps of: (i) forming the periodic arrangement by applying an electric field across a distribution of the particles in a curable liquid; and (ii) curing the curable liquid to form the matrix and thereby fixing the periodic arrangement of the particles. Also disclosed is a structural colour printing system suitable for carrying out the method of manufacture of the material.



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STRUCTURAL COLOUR MATERIALS AND METHODS FOR THEIR MANUFACTURE**BACKGROUND TO THE INVENTION****5 Field of the invention**

The present invention relates to structural colour materials, uses of such materials and methods for their manufacture. The invention has particular, but not exclusive, applicability to the fixing of structural colour materials, e.g. in the form of a printing process.

Related art

- 15 Natural opal is built up from domains consisting of monodisperse silica spheres of diameter 150-400 nm. These spheres are close-packed and therefore form a regular three dimensional lattice structure within each domain. The colour play (iridescence) of such opals is created by Bragg-like scattering of the incident light at the lattice planes of the domains.
- 20 US 2004/0253443 (equivalent to WO 03/025035) discloses moulded bodies formed from core-shell particles. Each particle is formed of a solid core, and the solid cores have a monodisperse particle size distribution. Each particle has a shell formed surrounding the core. The core and shell have different refractive indices. In one embodiment in this document, the core is formed of crosslinked polystyrene and the shell is formed of a
- 25 polyacrylate such as polymethyl methacrylate (PMMA). In this case, the core has a relatively high refractive index and the shell has a relatively low refractive index. A polymer interlayer may be provided between the core and shell, in order to adhere the shell to the core. Granules of the core-shell particles are heated and pressed to give a film. In this heating and pressing step shell material is flowable but the core material

remains solid. The cores form a three dimensional periodic lattice arrangement, and the shell material becomes a matrix material. The resultant material demonstrates an optical opalescent effect. Inorganic nanoparticles (e.g. metal nanoparticles or semiconductor nanoparticles) can be incorporated in the interstices between cores to provide enhanced
5 functionality to the material.

WO 2006/067482 discloses the use of an electric field to control the particle spacing of a regular lattice of particles having a monodisperse size. The particles were anionic polystyrene latex particles with an average diameter of 0.93 μm (polydispersity of 0.012).
10 The particles were dispersed in an aqueous solution at a concentration of 0.29 wt% at a KCl electrolyte concentration of 0.01 mM. A quadrupole electrode structure was used, in the form of four coplanar electrodes arranged around an observation region. A sinusoidal voltage signal was applied at a frequency of 1600 Hz. The voltage applied and the electrode structure allowed electric field strengths of up to about 30,000 $\text{V}_{\text{rms}}\text{m}^{-1}$
15 to be achieved. This treatment caused the particles to arrange into chains or spinning hexagonal close packed crystals, depending of the characteristics of the applied electric field. The spacing between the particles depended on the applied field strength. Without any electric field applied, the particles did not aggregate and random Brownian motion of the particles was observed. When an applied electric field was switched off, the
20 periodicity of the particles "dissolved", the arrangement of the particles once more becoming random. The proposed applications suggested in WO 2006/067482 are as a tunable optical filter for a CCD or other electronic image capturing device, relying on the tunability and reversibility of the periodic arrangement of particles.

25 WO 2009/060166 is a development from the disclosure of WO 2006/067482.
WO 2009/060166 discloses a similar method for controlling the particle spacing of a regular lattice of monodisperse particles in an aqueous solution. However, in WO 2009/060166, the electric field is applied between parallel electrodes, one of which is a

transparent electrode. Again, the suggested applications of WO 2009/060166 relate to the reversibility and tunability of the lattice.

- An explanation of the mechanism for the formation of periodic arrangements of particles in a liquid carrier under the influence of an electric field was disclosed by Elsner et al 2009 [Nils Elsner, C. Patrick Royall, Brian Vincent, and David R. E. Snoswell, "Simple models for two-dimensional tunable colloidal crystals in rotating ac electric fields" J. Chem. Phys. 130, 154901 (2009)].
- 10 Arsenault et al (2007) [André C. Arsenault, Daniel P. Puzzo, Ian Manners & Geoffrey A. Ozin "Photonic-crystal full-colour displays" Nature Photonics 1, 468 - 472 (2007)] disclose a full colour display technology based on thin films of monodisperse silica spheres. The silica spheres were made by sol-gel polymerization and are formed into an ordered array by convective self-assembly. The voids between the spheres were filled with a cross linkable low molecular weight PFS. This matrix component was then cross linked using UV. The spacing between the silica spheres could be changed using solvent swelling. Additionally, the spacing was affected by reversible electrochemical oxidation and reduction, controlled by an electric field. However, the silica spheres maintained their ordered array even when an electric field was not applied.
- 20 Kim et al (2009) [Hyoki Kim, Jianping Ge, Junhoi Kim, Sung-eun Choi, Hosuk Lee, Howon Lee, Wook Park, Yadong Yin & Sunghoon Kwon "Structural colour printing using a magnetically tunable and lithographically fixable photonic crystal" Nature Photonics 3, 534 - 540 (2009)] disclose a process for structural colour printing. Superparamagnetic colloidal nanocrystal clusters (CNCs) are capped with silica shells and dispersed in a mixture of solvation liquid and photocurable resin. Without an external applied magnetic field, the CNCs are randomly dispersed and display a brown colour, which is the intrinsic colour of magnetite. Under and external applied magnetic field, the CNCs assemble to form chain-like structures along the magnetic field lines. The attractive magnetic force
- 25

between the CNCs is balanced by repulsive electrostatic and solvation forces, the balance determining the interparticle distance.

In a film of the liquid material in Kim et al (2009), the required magnetic field is applied globally to the film. Then a required portion of the film is subjected to localised crosslinking by the application of UV radiation from a UV laser. When the magnetic field is removed, the assembly of the CNCs in the crosslinked region is fixed, but the CNCs in neighbouring regions become randomly dispersed once more. The process of magnetically aligning the particles and subsequently crosslinking the matrix takes a few seconds, but the crosslinking process itself is described as instantaneous, which leads to the presumption that the magnetic alignment is relatively slow.

After crosslinking of the required regions, the remaining liquid is washed away to leave isolated regions of ordered particles in the crosslinked matrix. This is necessary in Kim et al (2009) since the non-ordered parts of the film (even if crosslinked) have a brown colour. The brown colour is a result of the CNCs, which in this case are magnetite, but in practice any superparamagnetic material (typically a transition metal oxide) would have a relatively dark colour since such materials inherently absorb a significant proportion of incident light.

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SUMMARY OF THE INVENTION

The present inventors have realised that there are several fundamental drawbacks to the technology disclosed by Kim et al (2009). For example, the requirement for a strong magnetic field to achieve particle ordering, and the relatively slow particle ordering, limits the applicability of the technology disclosed by Kim et al (2009). Further limitations and drawbacks of that technology are identified below, with reference to specific preferred features of the present invention.

The present invention seeks to address one or more of these disadvantages. Preferably, the present invention reduces, ameliorates, avoids or even overcomes these disadvantages.

- 5 Accordingly, in a first aspect, the present invention provides a method of forming a periodic arrangement of particles distributed in a matrix, the refractive index of the material of the particles being different to the refractive index of the material of the matrix and the periodicity being such that, when illuminated with white light, the periodic arrangement provides structural colour, wherein the method includes the steps:
- 10 forming the periodic arrangement by applying an electric field across a distribution of the particles in a curable liquid; and
- curing the curable liquid to form the matrix and thereby fixing the periodic arrangement of the particles.
- 15 In a second aspect, the present invention provides a composite material having a periodic arrangement of particles distributed in a matrix, the refractive index of the material of the particles being different to the refractive index of the material of the matrix and the periodicity being such that, when illuminated with white light, the periodic arrangement provides structural colour, wherein the periodic arrangement of the particles
- 20 is formed (or is capable of being formed) by applying an electric field across a distribution of the particles in a curable liquid and the matrix is formed by curing the curable liquid to thereby fix the periodic arrangement of the particles.

In a third aspect, the present invention provides a use of the composite material of the

25 second aspect in order to display a structural colour arrangement.

In a fourth aspect, the present invention provides a structural colour printing system having a printer head with electric field application means, the system further having an

irradiation source, wherein the system is adapted to form a localised fixed periodic arrangement of particles distributed in a matrix by:

applying an electric field across a distribution of the particles in a curable liquid using the electric field application means; and

- 5 applying curing radiation to the curable liquid by operation of the irradiation source to form the matrix, thereby fixing the periodic arrangement of the particles.

Any aspect of the invention may be combined with any other aspect of the invention.

- 10 Preferred (or simply optional) features of the invention will now be set out. These are applicable singly or in any combination with any aspect of the invention, unless the context demands otherwise.

- The composite material (considered here to be the material after curing of the matrix)
- 15 may be provided as a component in sheet or film form. Alternatively, the composite material may be provided as a component in filament form. Typically, at least one linear dimension (e.g. thickness) of the component is relatively small, in order that a suitable electric field strength can be applied across the component using an acceptably low voltage. One (in the case of a filament) or two (in the case of a sheet or film) orthogonal
- 20 linear dimensions of the component may be at least 10 times greater (more preferably at least 100 times, 1000 times or 10000 times greater) than the thickness of the component, since these other dimensions of the component are not subject to the same limitation as the thickness and it is typically of interest to provide a macroscopic scale pattern of structural colour in the component.

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Preferably, the refractive index of the material of the particles is the bulk refractive index for the material from which the particles are formed. Similarly, preferably the refractive index of the material of the matrix is the bulk refractive index for the material from which the matrix is formed. It is considered that the refractive index of the particles is not

significantly affected by the size of the particles, particularly for hydrophobic polymers, and so it is convenient here to refer to the bulk refractive indices.

Preferably, the modulus of the refractive index difference between the refractive indices of the materials of the particles and the matrix is at least 0.05. More preferably, this difference is at least 0.1. Still more preferably, this difference is at least 0.11, more preferably at least 0.12, more preferably at least 0.13, more preferably at least 0.14 or more preferably at least 0.15. The effect of increasing modulus of refractive index difference is improved reflection of incident light from the boundary between the matrix and the particles. This in turn improves the Bragg reflection effects and so enhances the spectral colour response of the material.

Although it is the modulus of the refractive index difference between the particles and the matrix which is of primary interest in the present invention, it is convenient to refer to preferred ranges for absolute values of the refractive indices for these components. Preferably, the refractive index of the material of the particles is at least 1.5. More preferably, this refractive index is at least 1.51. Still more preferably, this refractive index is at least 1.52, more preferably at least 1.53, more preferably at least 1.54, more preferably at least 1.55, more preferably at least 1.56, more preferably at least 1.57, more preferably at least 1.58.

Preferably, the refractive index of the material of the matrix is at most 1.48. More preferably, this refractive index is at most 1.47. Still more preferably, this refractive index is at most 1.46, or more preferably at most 1.45.

In the discussion above, it is assumed that the refractive index of the particles is higher than that of the matrix. However, it is possible for the refractive index of the particles to be lower than that of the matrix. In that case, the above preferred refractive limitations for the particles can be applied to the matrix and vice versa. Thus, the matrix may be

formed of a relatively high refractive index material, such as an ionic liquid. For example, a suitable material is 1-butyl-3-methylimidazolium iodide, which has a refractive index of 1.57.

- 5 Preferably the material of the particles is not ferromagnetic or superparamagnetic. Such materials typically are strong absorbers of light, which provides performance limitations on the optical quality of the material.

The ordering of the particles in the liquid (and in the subsequent matrix) may be one
10 dimensional ordering. In this way, the particles preferably are ordered into elongate chains of particles. The chains typically orient with their principal axes parallel to the direction of the field lines of the electric field. The inter-particle spacing in the chains is typically determined by the electric field strength. The ordering of the particles in the liquid may be two dimensional or three dimensional. This can occur by the chains of
15 particles aligning with each other.

It is possible to use a dc electric field in order to provide ordering of the particles in the curable liquid. However, there is a risk with using a dc electric field that parallel
conduction may be provided through ions in the matrix component and electrochemical
20 breakdown at one electrode. In order to avoid this, low dc electric field strengths can be used, relying on electrophoresis to provide ordering, but in this case the ordering can be relatively slow. In this case, the preferred dc electric field strength is at least 100 V/m, more preferably at least 1000 V/m.

- 25 Preferably, though, an ac electric field is used, since this can allow for very fast ordering of the particles. A continuously varying signal is preferred, e.g. a sinusoidal signal. The frequency is preferably at least 1 kHz, more preferably at least 10 kHz, more preferably at least 100 kHz. The frequency is preferably at most 1 MHz, more preferably at most 500 kHz. The ac electric field strength is typically at least 10,000 Vrms/m, more

preferably at least 100,000 Vrms/m. For example, an ac electric field strength of about 1,000,000 Vrms/m may be suitable.

In order to provide enhanced ordering of the particles in the matrix under the influence of the applied electric field, it is preferred to use materials for the particles and for the matrix that have significantly different dielectric constants. However, it has been found that when the particles are formed from materials having particularly high dielectric constants, the particles tend to aggregate in the liquid before the electric field is applied. In that case, it is difficult to form the periodic structure. Thus, a balance should be found between providing a suitable degree of contrast in dielectric constant and avoiding aggregation of the particles.

Preferably, the dielectric constant of the matrix component is at least 10. This compares with the dielectric constant of water of about 80, but as mentioned elsewhere herein, it is difficult to provide a curable matrix component with a suitable refractive index and a high dielectric constant. The dielectric constant of the material of the particles is preferably less than 10, more preferably less than 8. Providing a suitable difference in dielectric constant between the particles and the matrix assists in suitable ordering of the particles on application of the electric field.

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It is noted here that the principle of electric field ordering of particles in a liquid has been demonstrated in, for example, WO 2006/067482 and WO 2009/060166. However, those earlier disclosures provided only the ordering of particles in an aqueous solution. In the preferred embodiments of the present application, the particles are first ordered in the liquid and then the liquid is cured (e.g. by crosslinking), in order to fix the periodic arrangement of the particles in a solid matrix. Preferably, curing is carried out by UV irradiation (or other irradiation) or by other means, e.g. by thermal curing. Thus, the requirement for a curable liquid is a significant one – the liquid must be both curable and

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provide suitable refractive index and dielectric contrast with the particles. The suspension must also form a stable dispersion with no aggregates.

Preferably, the liquid includes a prepolymer component. The prepolymer may be a monomer or an oligomer. For example, the prepolymer component may be a straight chain structure or a branched structure. Straight chain structures tend to have a lower refractive index than ring structures (for similar molecular weight). For example, the prepolymer may be ethoxylated trimethylolpropane triacrylate having a refractive index of 1.47. As will be clear to the skilled person, one or more other suitable prepolymers may be used. The selection of the prepolymer depends at least in part on the stability of the suspension of the particles in the liquid, and thus depends on the material of the particles. However, suitable combinations can be tested and assessed by the skilled person with ease. Suitable matrix materials with relatively low refractive indices are listed at http://www.texloc.com/closet/cl_refractiveindex.html (accessed 9 March 2011). For example, poly(ethylene glycol) has a refractive index of 1.46. Other ethylene glycol polymers can be used. Other suitable materials for the matrix are disclosed in US 2005/0142343, the content of which is incorporated herein by reference in its entirety and particularly the content in relation to suitable materials for the matrix material (also referred to in US 2005/0142343 as the "shell material"). Suitable low refractive index materials include polyethylene, polypropylene, polyethylene oxide, polyacrylates, polymethacrylates, polybutadiene, polymethyl methacrylate, polytetrafluoroethylene, polyoxymethylene, polyesters, polyamides, polyepoxides, polyurethane, rubber, polyacrylonitrile and polyisoprene, for example. Further suitable materials for the matrix are disclosed in US 2005/0228072, the content of which is incorporated herein by reference in its entirety and particularly the content in relation to suitable materials for the matrix material (also referred to in US 2005/0228072 as the "shell material").

The liquid typically further includes a photoinitiator in order to interact with UV in order to provide curing of the liquid to form the solid matrix. A suitable photoinitiator is 2,2

dimethoxy-2-phenylacetophenone. Further suitable photoinitiators are listed in the brochure "Photoinitiators for UV Curing (Key Products Selection Guide 2003)" Edition 2003 from Ciba Speciality Chemicals, document g-48/2003 (October 2003), the content of which is hereby incorporated by reference in its entirety. Further suitable
5 photoinitiators are Norrish type I initiators and Norrish type II initiators.

The liquid may further include one or more organic solvents in order to blend with the prepolymer component. This has the effect of reducing the viscosity of the liquid, to allow faster and more effective formation of the periodic structure. In some embodiments,
10 it may also allow the refractive index of the liquid to be tailored to a suitable value. For example, the organic solvents may be selected from methyl ethyl ketone (refractive index of 1.38) and ethanol (refractive index of 1.36). The amount of solvent is typically at least 10% by volume, more preferably at least 20%. The amount of solvent may be up to about 50% by volume, more preferably up to about 40% by volume. Additionally or
15 alternatively, the addition of the solvent may provide enhanced dielectric constant contrast between the matrix and the particles.

In some embodiments, it is positively preferred not to include any solvent in the matrix component, particularly volatile solvents. The reason for this is that, even after curing of
20 the matrix, some of the solvent can be lost from the matrix. This in turn can give rise to some de-swelling of the matrix, and therefore to a change in the periodic spacing of the particles over time. This is disadvantageous in cases where there is a particular required colour of the structural colour. Thus, in some embodiments, preferably the liquid (which forms the matrix) consists only of a crosslinkable material.

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Preferably, the liquid is non-aqueous. Although an aqueous liquid may be advantageous in terms of providing good dielectric constant differentiation with suitable particles, and/or good refractive index differentiation with suitable particles, it is difficult to provide an

aqueous liquid that can be solidified in a short time frame in order to "freeze" the order applied to the particles.

Preferably, the viscosity of the liquid (before curing) is at most 100 centipoise at 25°C.

- 5 Using a liquid with higher viscosity than this would tend to result in slower formation of the periodic arrangement of the particles. For this reason, the viscosity of the liquid (before curing) is preferably at most 50 centipoise, more preferably at most 10 centipoise. It is, however, considered that moderate viscosity may extend in a useful manner the thickness of the structure that may be formed. Without wishing to be bound by theory, it
- 10 is considered that using a liquid with moderate viscosity may dampen ion induced flows that would otherwise disrupt the chains of particles that form under the influence of the applied electric field.

- Preferably, the method includes the step of applying the electric field at a localised region,
- 15 thereby forming only a localised region of the periodic arrangement of particles in the liquid, adjacent a region of randomly dispersed particles in the liquid. Subsequently, both the localised region and the adjacent region are preferably subjected to curing in order to form the matrix material. In this way, the present invention preferably provides a means for effectively printing structural colour in the material, in which the structural colour is
- 20 provided only at the localised region but the cross linking is carried out more widely than this. It is preferred to cross link both the ordered and the disordered regions of the material, in order to provide the component with suitable rigidity, e.g. in the form of a sheet or a fibre.

- 25 It is to be noted that the application of the electric field does not significantly affect the composition of the composite material. Similarly, curing does not significantly affect the composition of the material. Thus, after curing, preferably the composition of the ordered region and the composition of the disordered region is substantially identical.

It is preferred that the finished component comprises a fibre, sheet or film having substantially uniform thickness. Preferably, the disordered region is present in the sheet or film, providing a mechanical link between ordered regions.

- 5 Where the composite material is treated (e.g. by irradiation with the curing radiation) in order to cure the liquid, it is possible to treat each required region locally. In the case of the printer system, the irradiation source may be provided as part of the printer head. Alternatively, it is possible to irradiate the whole product in a single step.
- 10 Thus, preferably, the fixed periodic arrangement of the particles distributed in a matrix is localised in the sense that the fixed periodic arrangement is formed at a first region in the material and that in a second region, adjacent the first region, the arrangement of particles is substantially random. It is possible for each of the electric field and the curing radiation to be applied only at the first region (and thus not at the second region) and a
- 15 particular time. However, in some embodiments, it is possible for one of the electric field and the curing radiation to be applied to both the first and second regions, provided that the other of the curing radiation and the electric field is applied only to the first region. Since the curing radiation and the electric field cooperate to provide a fixed periodic arrangement of the particles, the second region either does not become cured (because
- 20 curing radiation is not applied) and so any periodic arrangement of the particles due to an applied electric field is lost when the electric field is removed, or the second region does not have a suitable electric field applied, and so the application of the curing radiation simply fixes a substantially random arrangement of the particles in the matrix. In some embodiments, it can be advantageous to operate one of the irradiation source and the
- 25 electric field application means so that both the first and second regions are subjected to the curing radiation or the electric field, because this allows the system to be operated efficiently because it is not necessary to scan the electric field application means or the irradiation means. In other embodiments, it can be advantageous to apply both the curing radiation and the electric field only to the first region and not to the second region

at any one time, because this allows the printing system to print in a pixellated fashion, so that the flexibility of the printing system is improved.

The structural colour provided due to the ordering of the particles depends on the particle-to-particle spacing, i.e. the periodicity. This in turn depends (at least in part) on the electric field strength applied in order to form the periodicity. It is preferred that there is provided a third region in the material, optionally adjacent the first and/or second region, and the third region optionally has a different structural colour to the first region. The different structural colour in the third region is caused by a different periodicity of the particles in the third region compared with the particles in the first region. The different periodicity may be manifested by a different particle-to-particle spacing in the third region compared with the first region. This may be provided by the application of a different electric field strength at the third region compared with the second region.

It is preferred that the electric field is applied to the first and third regions by an electric field application means that is movable with respect to the material. In that case, preferably the different electric field strength at the third region is applied by suitable control of the electric field application means at the first region and then subsequently at the third region.

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Preferably, the composite material is formed from materials having relatively low optical absorbance. However, the presence of particles of size of the order of the wavelength of light causes scattering of light in the composite material, and so the composite material is typically not transparent. Absorbance of a sample of a material is defined as A_λ :

$$A_\lambda = \log_{10} \left(\frac{I_0}{I} \right)$$

where I_0 is the light intensity before entering the sample and I is the intensity of light that is transmitted by the sample, and the proportion of the incident light absorbed by the sample is proportional to its thickness L . Measurements are taken at room temperature

using a wavelength of green light. Therefore a measure of the light-absorbing properties of a material is the parameter A_λ/L .

Preferably, for the bulk material of the particles, A_λ/L is not more than 0.1/cm.

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Preferably, for the bulk material of the matrix, A_λ/L is not more than 0.1/cm.

It is noted that the resultant component typically has a relatively light, e.g. white, colour at disordered regions. This is due to random scattering from the particles at the random regions. The low light absorption of the materials of the particles and the matrix allows the disordered regions to scatter and reflect light, rather than absorb it to a significant degree. This can help to provide good contrast with the regions having structural colour. It is noted here that the use of transition metal compositions (e.g. for ferromagnetic or superparamagnetic particles) leads to a high light absorption and therefore a relatively low contrast between the random order regions and the ordered regions of the component. The use of such materials also places a severe restriction on the allowable thickness of the component.

Preferably, the thickness of the composite material corresponds to the length of an ordered array of particles, aligned in the thickness direction of the material, of at least 10 particles. More preferably, this thickness corresponds to at least 20, at least 30, at least 40 or at least 50 particles. Preferably, the thickness of the composite material corresponds to the length of an ordered array of particles, aligned in the thickness direction of the material, of at most 1000 particles. More preferably, this thickness corresponds to at most 500, at most 200, or at most 100 particles. This thickness therefore corresponds to the number of layers of particles in the ordered arrangement through the thickness of the composite material. It is considered that the structural colour effect increases with the number of layers. However, this must be balanced against the voltage needed to provide the required electric field strength across the

material. Of course, where a particularly thick component is required with structural colour, it would be possible to form individual layers with the required arrangement of structural colour and then laminate these layers to form the final component, the respective arrangements of structural colour in each layer being aligned in register with each other.

Preferably, the particles have a mean particle diameter in the range from about 5 nm to about 2000 nm. More preferably, the particles have a mean particle diameter in the region of about 50-500 nm, more preferably 100-500 nm. Still more preferably, the particles have a mean particle diameter of at least 150 nm. The particles may have a mean particle diameter of at most 400 nm, or at most 300 nm, or at most 250 nm.

Preferably the polydispersity of the particles is at most 5%. However, the inventors consider that one advantage of some embodiments of the present invention is that they are more tolerant of polydispersity of the particle size than previous methods for achieving structural colour.

It is preferred that the particles do not agglomerate in use. This allows the particles to be more easily ordered into the required periodicity in order to achieve structural colour.

The degree of agglomeration can be assessed using dynamic light scattering (DLS) particle size analysis. Non-agglomerating particles therefore provide a stable colloid of the particles in the liquid. One means of providing a stable colloid is to provide charged particles, the electrostatic repulsion between the particles mitigating against agglomeration. Additionally or alternatively, sterical hindrance effects can mitigate against agglomeration. These principles are well understood by the skilled person. For example, the synthesis of charged monodisperse polystyrene colloidal particles is disclosed in Reese et al (2000) [Chad E. Reese, Carol D. Guerrero, Jesse M. Weissman, Kangtaek Lee and Sanford A. Asher, Synthesis of Highly Charged, Monodisperse Polystyrene Colloidal Particles for the Fabrication of Photonic Crystals, Journal of Colloid

and Interface Science, Volume 232, Issue 1, 1 December 2000, Pages 76-80]. The particle charge densities can be determined by conductometric titration, allowing the charge per particle to be determined. Further detail on the preparation of polymer dispersions is set out in Taylor (2002) [Mike A. Taylor, Synthesis of Polymer Dispersions, Chapter 2 of Polymer Dispersions and Their Industrial Applications, Edited by Dieter Urban and Koichi Takamura, Wiley-VCH Verlag GmbH & Co. KGaA ISBN 3-527-30286-7]. As is known to the skilled person, the incorporation of acid groups into the material of the particles allows the particles to form a stable colloidal suspension. Suitable particles include carboxylated latex beads available from Aldrich, or the Reese et al (2000) polystyrene particles mentioned above.

Preferably, the thickness of the sheet is at least 10 μm . The thickness of the sheet may be up to 1 mm, but is more preferably not more than 500 μm .

The electric field is applied by a suitable arrangement of electrodes. For example, respective electrode may be provided on one side of the composite material. More preferably, respective electrodes are provided on opposed sides of the composite material.

For each localised region to be treated with the electric field, preferably the electric field is applied for not more than 100 ms, more preferably not more than 50 ms, more preferably not more than 10 ms. Applying the electric field for only a short time can still provide the required periodicity of the particles. This is highly advantageous, because it means that the required structural colour can be formed at each region very quickly. This lends itself particularly well to a rastering-based pixel-by-pixel printing process. It is considered that the process of Kim et al (2009) is particularly unsuited to such a process, in view of the relatively long time scale for the corresponding magnetic alignment.

Preferably, in the finished printed sheet, the regions treated with the electric field form coloured regions and the remainder of the sheet provides a substantially white background.

- 5 The composite sheet material, once printed, is particularly suitable for use in security applications. For example, the material can be incorporated into banknotes or other financial instruments. The material may also be used in security labelling applications, e.g. to demonstrate the authenticity of a product.
- 10 Further optional features of the invention are set out below.

BRIEF DESCRIPTION OF THE DRAWINGS

- The preferred embodiments of the invention are described below by way of example, with reference to the drawings, in which:

Fig. 1 shows a schematic cross sectional view of the formation of ordered chains of particles in a region between two electrodes, and disordered adjacent regions.

Fig. 2a shows a scanning electron microscope image of a cross section of a composite material according to an embodiment of the invention.

- 20 Fig. 2b shows a further magnified view of the cross section of Fig, 2a.

Fig. 3 shows a plot of wavelength vs intensity obtained in back scattering mode for samples cured under different applied electric field strengths. A reference plot is included for a sample cured under zero applied electric field strength.

- 25 Fig. 4 shows a plot of the position of the peak intensity (measured as shown in Fig. 3) for samples cured under different applied electric field strengths.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS, FURTHER
OPTIONAL FEATURES OF THE INVENTION**

The present inventors have demonstrated the formation of permanent structural colour
5 by assembly of colloidal particles in an alternating electric field. Particles form strings in
a liquid medium by dipole-induced chaining and are then fixed in place by photochemical
curing of the liquid medium. The strength of the electric field controls the separation of
the non-touching particles giving control of the colour. Even at the time of writing when
the invention has not been optimised, structure formation and curing occur within
10 seconds promising a simple, fast and scalable route for patterning structural colour.

Structural colours arise from the diffraction properties of periodic structures on the sub-
micron scale. Examples from nature include a peacock's feathers and the wings of the
Morpho butterfly [Description Refs 1 and 2]. Structural colour is highly saturated, fade
15 resistant and non-toxic comparing favourably with traditional dyes and pigments.
Colloidal crystals have the potential to provide a low-cost route to realising large scale
production of structural colour by Bragg diffraction and have been explored for this
purpose. Several methods have been demonstrated for assembling colloidal crystals
[Description Refs 3, 4, 5, 6]. A key to generating tunable structural colour from one
20 colloidal system (an aim often referred to as 'one-pot colour') is the ability to adjust the
lattice spacing of non-touching spheres. In close packed colloidal crystals lattice spacing
is set by the diameter of the colloidal particle. Various composites with expandable
materials between the interstices of the colloidal crystal can reversibly expand and
contract as a way of mediating the lattice spacing and therefore observed colour
25 [Description Refs 5 and 7].

Recently studies have focused on magnetic fields to form strings of superparamagnetic
colloidal particles which are then fixed in place by UV curing. Particle separation can be
controlled by swelling the matrix with a hygroscopic salt⁸ or adjusting the magnetic field

strength before curing [Description Ref 4]. Printing of a range of structural colours has been demonstrated with magnetic colloidal particles but light absorption by the magnetic core of the colloidal particle inevitably reduces the intensity of the observed colour.

- 5 Here the present inventors disclose a method for creating permanent and tunable structural colour using polystyrene colloidal particles (low light-absorbance) and electric fields. Previous research has demonstrated alignment of colloidal particles in an alternating electric field [Description Refs 9, 10, 11]. Transitory dipoles induced in each colloidal particle cause them to align parallel to the field lines.
- 10 Dielectric particles in electric fields experience a charge separation of positive and negative components. The resulting effective dipole moment ρ_{eff} of a homogeneous dielectric sphere can be calculated from the effective field strength E_{rms} [Description Ref 14]:

$$\rho_{eff} = 4\pi\epsilon_p K(\omega) R^3 E_{rms} \quad (1)$$

- 15 In this equation (1), ϵ_p stands for the particle's relative permittivity, R for its radius and ω denotes the angular frequency of the AC field (the case of a DC field is covered for $\omega = 0$). $K(\omega)$ is the Clausius-Mosotti function, which quantifies the conductivity/permittivity contrast between particle and medium and is (simplified) given by:

$$K(\omega) = \begin{cases} \frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m}, & \omega < \omega^* \\ \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}, & \omega \geq \omega^* \end{cases} \quad (2)$$

- 20 At low frequencies, the Clausius-Mosotti factor is calculated from the conductivities of surrounding medium (σ_m) and particle (σ_p), in the regime of high frequencies it is calculated from the respective relative permittivities ϵ_m and ϵ_p . The Clausius-Mosotti function is limited to values between $-0,5$ and $+1$. The two regimes are divided by the crossover frequency:

$$\omega^* = \frac{1}{2\pi\epsilon_0} \sqrt{\frac{\sigma_p^2 - 2\sigma_p\sigma_m + 2\sigma_m^2}{\epsilon_p^2 - 2\epsilon_p\epsilon_m + 2\epsilon_m^2}} \quad (3)$$

with the vacuum permittivity ϵ_0 .

The field-induced dipoles interact with each other as well as the external electric field.

- 5 These dipole-dipole and dipole-field interactions can lead to attractive and repulsive forces. The most relevant forces for the electric field alignment are [Description Ref 14]:

- The chaining force, that assembles the spheres in rod-like structures:

$$F_{chain} \propto -\pi\epsilon_m K(\omega)^2 R^2 E_{rms}^2 \quad (4)$$

10

- The dielectrophoretic force (DEP), that shifts the dipoles in non-uniform electric fields towards (positive dielectrophoresis, $\epsilon_p > \epsilon_m$) or away from (negative dielectrophoresis, $\epsilon_p < \epsilon_m$) intensity maxima:

$$F_{DEP} = 2\pi\epsilon_m K(\omega) R^3 \nabla E_{rms}^2 \quad (5)$$

- 15 This technique has also been used to assemble colloidal gold and carbon nanotubes into wires [Description Ref 13].

In cases where a soft repulsive force is present between particles, such as an electrostatic force, separation between colloidal particles can be adjusted by changing
20 the amplitude of the electric field. With 1 μm polystyrene particles in water a range of 150nm surface to surface particle separation was achieved [Description Ref 10].

However any structure which formed, in previous research, was lost when the field was switched off as the chains dissipated under Brownian motion.

In the present work, the inventors have created permanent structural colour using the dipole chaining effect in an AC field and fixation of the colloidal particles with a UV curable solution.

5 Colloidal particles were synthesised as follows. The syntheses were conducted in a 1L glass reactor equipped with condenser, mechanical stirrer and inert gas inlet at a temperature of 75°C. A precision piston pump (ProMinent Dosiertchnik AG, type micro g/5) was used to add the monomer emulsions dropwise. The monomer styrene (BASF SE) was distilled under reduced pressure prior to use. Butanediol diacrylate (BASF SE)
10 was passed over an ion exchange column (Dehibit 200, PolymerScience) for the removal of the inhibitor. Methacrylic acid (Sigma Aldrich) was used as delivered. Dowfax 2A1 (The Dow Chemical Company), was provided by Nordmann, Rassmann GmbH. Dowfax and all other chemicals (Sigma Aldrich) were used as provided. The demineralised water was saturated with nitrogen prior to use.

15

A mixture of 0.29g sodium dodecylsulfate, 300g of water, 3.6g of styrene and 0.4g of butanediol diacrylate was filled into the reactor and subsequently the reaction was initiated by the addition of 0.1g of sodiumdisulfite and 0.17g sodiumpersulfate, each dissolved in 5g of water. The observation of cloudiness after 8min indicated the
20 formation of seed particles. After additional 15min a monomer emulsion consisting of 0.3g of sodiumdodecylsulfate, 0.1g of potassium hydroxide, 0,45g Dowfax 2A1, 140g of water, 105g of styrene and 10.5g of butanediol diacrylate was added dropwise at a rate of 0.8 mL/min. 30 min after the end of the addition, a solution of 0.1g sodiumpersulfate in 5g of water was added.

25

Then a second monomer emulsion, consisting of 0.12g of sodiumpersulfate, 0.08g of Dowfax 2A1, 58g of water, 49g of styrene, 5g of butanediol diacrylate and 10.8g of methacrylic acid was added dropwise at a rate of 0.9 mL/min. After the addition was finished the latex was stirred for another 60min to reduce possible monomer residues.

The resultant colloidal particles were polystyrene(co-methacrylic acid) colloidal particles (refractive index $\sim 1.48 - 1.51$). The refractive index was slightly lower than expected, this being considered to be due to some slight swelling of the particles (without wishing to be bound by theory). These particles were dispersed in a solution of solvent (methylethylketone (25 wt%) (refractive index 1.38, dielectric constant 18.5, room temperature viscosity 0.4 centipoise)), photoinitiator (2,2-dimethoxy-2-phenylacetophenone)(5 wt%) and a monomer (or pre-polymer) in this case Sartomer SR454 (70 wt%) (refractive index 1.47, dielectric constant 2-6, room temperature viscosity 62 centipoise). The refractive index of the liquid component was 1.44. . The refractive index contrast (modulus of the difference between the refractive index of the particles and the matrix) was 0.16.

Sartomer SR454 is a fast curing commercially available monomer which undergoes free radical polymerisation in UV light. It is a branched molecule having low refractive index SR454 is ethoxylated trimethylolpropane triacrylate.

The colloid was found to be stable over several weeks at room temperature. A colloidal particle diameter of 230 ± 16 nm was determined by dynamic light scattering (DLS). The magnitude of the dipole chaining forces was found to be highly dependent on the difference in polarisability between the medium and the colloidal particle. Previous work was in high dielectric constant solvents such as water so one challenge in this system was to find a UV curable medium with a sufficiently high dielectric constant for strings of particles to form. The inventors found that by adding methyl ether ketone, which was miscible (i.e. soluble) with the Sartomer SR454 UV monomer, the overall dielectric constant of the medium was raised enough for dipole induced particle alignment to occur.

In this example, patterned ITO electrodes were used. These were cleaned with isopropanol and distilled water before drying with a nitrogen gun. To form a cell, a 5 μ L

drop of the colloid was sandwiched between two electrodes. By measuring with a digital screw micrometer and SEM, the inventors found a reproducible cell thickness of about 20 μ m. Under optical microscope illumination, diffraction rings were observed on application of an electric field between $0.8 \times 10^6 \text{V}_{\text{RMS}}\text{m}^{-1}$ and $2 \times 10^6 \text{V}_{\text{RMS}}\text{m}^{-1}$ at 100kHz.

- 5 Voltages higher than this caused electrolysis of the solution. The switching time of this crystal structure formation in water has previously been measured to be 0.5ms [WO 2006/067482 and WO 2009/060166]. With the polymeric component liquid used here, the chaining time is considered to be well below 100 ms. With the electric field applied across the cell the liquid was cured by exposure to 395nm UV light, as illustrated
- 10 schematically in Fig. 1, until the liquid was sufficiently cured for the resultant sheet to be able to be free standing.

Fig. 1 shows a schematic view of the formation of strings of colloidal particles in a layer 10 of the liquid containing the particles 12. A first region 14 of the layer 10 is placed in

15 close proximity to upper 16 and lower 18 electrodes. The first region is then subjected to an alternating electric field by suitable operation of voltage source 20. The result is that strings 22 of the particles form in the first region 14. No such ordering is provided in the second region 24, adjacent the first region. It is found that diffraction rings are produced by applying the aligned colloids in the alternating electric field. UV light is then used to fix

20 the particle structure in place by free radical polymerisation of the monomer SR454 in solution. The resultant film was about 20 μ m thick and was substantially free standing. The resultant film demonstrated structural colour in the first region (a rectangular shape, of maximum width about 5 mm, surrounded by a white background (the second, non-ordered region).

25

A cross-section of a cured film was made by microtoming and coated with several nm of Au for imaging by scanning electron microscopy (Figs. 2a and 2b). The formation of strings of colloidal particles, and voids where they have been removed during microtoming, is clearly visible. More specifically, Fig. 2a shows a scanning electron

microscope image of the cross section of the cured films after sputtering of a Au layer. Fig. 2b shows a scanning electron microscope image of the same sample (see boxed region of Fig. 2a) at greater magnification. This shows the formation of strings of colloidal particles within the matrix. Dark cavities are where particles have been removed during microtoming. In these images, Fig. 2a has a scale bar of 2 μm and Fig. 2b has a scale bar of 1 μm .

To show the possibility of tuning colour, films were cured at different electric field strengths and the results illustrated in Figs. 3 and 4.

10 Different samples were cured at different applied electric field strengths. The cell thickness was approximately constant for the samples. In Fig. 3, the plot is of backscattered intensity. There is a red shift in the spectral signature for lower voltages, as indicated by Fig. 4. Macro photographs (not shown, but at fixed angle) of illuminated films produced at high and low field strength revealed different structural colours.

15

At higher field strengths the colour was shifted towards the blue end of the spectrum (at a fixed angle of incidence and viewing angle). This can be understood from a simple diffraction argument – the smaller interparticle separation at higher field strength gives a smaller optical path length between light scattered from successive colloidal particles resulting in constructive interference of the shorter wavelength light.

20

Although the example set out above provided a component in the form of a sheet or a film, it is possible to form the component as a filament or fibre. Such components may be subjected to further processing, e.g. to form a woven or nonwoven article.

25

In another example, ethanol is used to replace some or all of the methyl ether ketone. Ethanol has a refractive index of 1.36, so can assist in reducing the overall refractive index of the matrix.

In another example, the refractive index of the particles is lower than that of the matrix. Thus, the matrix may be formed of a relatively high refractive index material, such as an ionic liquid, one suitable example being 1-butyl-3-methylimidazolium iodide, which has a refractive index of 1.57.

5

In another example, the polymer component is a blend of compositions. Sartomer 256 is blended with Sartomer 454 of the main example.

10 In another example, a thermally cross-linkable polymer component is used. Suitable polymer components will be known to the skilled person.

15 In another example, the particles are ordered by applying a dc voltage. dc ordering relies on electrophoresis and typically takes a minute or two for the particles to migrate and pack. Very low voltages can be used, and thus negligible currents. It is possible to stay below the voltages that activate electrochemistry at the electrodes (1-3 volts). The present inventors found that in the materials system discussed in the main example above, where the electrode is formed ITO, the threshold voltage was 2.0 volts dc. Below this threshold the particles can be moved without degrading the ITO electrodes (in aqueous fluid). In this example, the electrode separation was typically 1-2mm so the applied voltage provided very low field strengths compared to AC induced chaining, i.e. about 1×10^3 V/m compared to about 1×10^6 V_{RMS}/m for AC induced chaining.

20

The preferred embodiments can be put into effect using a structural colour printing system (not shown). The printing system has a printer head with electric field application means in the form of an electrode arrangement and voltage supply. The printer head also has a UV source. The printer head has an actuator to move the printer head with respect to a sheet (or filament) of the colloid. The printer system can therefore form a localised fixed periodic arrangement of particles distributed in the matrix by movement of the printer head to a required first region of the sheet and applying a suitable electric field

25

(tuned to provide the required structural colour at the first region) across the distribution of the particles in the curable liquid. Substantially simultaneously, the UV source is operated to apply curing radiation to the curable liquid at the first region to form the matrix and thereby fixing the periodic arrangement of the particles. The UV source in this
5 embodiment may be a UV laser or UV LED, for example.

In a modification of this embodiment, the UV source may apply the required curing radiation to both the first region (ordered) and the second region (disordered) at the same time. This can lead to faster throughput printing, particular where large areas of
10 second region are required.

In a still further modification, the electric field application means may be structured to provide a particular pattern, e.g. using an electrode having a particular pattern. This is of interest in particular for security labelling applications of the invention.

15 In summary, the present inventors have demonstrated a new technique for creating structural colour by assembling strings of colloidal particles in an alternating electric field before fixing the structure by UV curing. Colour can be tuned by adjusting the field strength and thereby the inter-particle separation. To increase the intensity of the colour
20 formed, it is of interest to increase the refractive index contrast between the colloidal particle and cured matrix. This can be achieved, for example, by doping of the colloid with high refractive index nanoparticles such as zinc oxide. The research presented is promising for the commercialisation of printed structural colour for display applications and also for security applications, e.g. as a security label, tag or other security device.

25 As will be clear to the skilled person, on the basis of this disclosure, a large number of permutations of particle compositions, liquid compositions and UV initiators can be used, each of which can achieve the technical benefit of the invention. However, based on the work reported here, it is possible to list some general requirements for the preferred

embodiments. The particles (and the UV initiator) should form stable, monodisperse dispersion in the UV curable liquid. The particles and the liquid should have sufficient dielectric contrast and/or conductivity contrast to form non-touching particle chains that produce structural colour on application of an electric field. In operation, the maximum
5 electric field strength used to form the required periodicity should be below the dielectric breakdown potential of the suspension, in order to avoid damaging the electrodes or causing unwanted electrochemical reactions. The UV curing process should not disrupt the particle chain formation (or other periodicity). Additionally, the particle periodicity (chains, etc.) should remain intact after curing so that, after curing, there is no longer any
10 requirement for the electric field to be present in order for the composition to display structural colour.

The preferred embodiments have been described by way of example. Modifications of these embodiments, further embodiments and modifications thereof will be apparent to
15 the skilled person on reading this disclosure and as such are within the scope of the invention.

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CLAIMS

1. A method of forming a periodic arrangement of particles distributed in a matrix,
the refractive index of the material of the particles being different to the refractive index of
5 the material of the matrix and the periodicity being such that, when illuminated with white
light, the periodic arrangement provides structural colour, wherein the method includes
the steps:
forming the periodic arrangement by applying an electric field across a distribution
of the particles in a curable liquid; and
10 curing the curable liquid to form the matrix and thereby fixing the periodic
arrangement of the particles.
2. A method according to claim 1 wherein the modulus of the refractive index
difference between the refractive indices of the materials of the particles and the matrix is
15 at least 0.05.
3. A method according to claim 1 or claim 2 wherein the ordering of the particles in
the liquid is at least one dimensional ordering.
- 20 4. A method according to any one of claims 1 to 3 wherein the spacing of the
particles in the periodic arrangement is varied by varying the electric field strength.
5. A method according to any one of claims 1 to 4 wherein the electric field is an ac
electric field of frequency at least 1 kHz.
- 25 6. A method according to any one of claims 1 to 5 wherein the liquid is non-aqueous.
7. A method according to any one of claims 1 to 6 wherein the dielectric constant of
one of the matrix component and the material of the particles is at least 10 and the

dielectric constant of the other of the matrix component and the material of the particles is less than 10.

8. A method according to any one of claims 1 to 7 wherein the curing step is carried out by applying curing radiation.

9. A method according to any one of claims 1 to 8 wherein the liquid further includes a photoinitiator in order to interact with the curing radiation in order to provide curing of the liquid.

10

10. A method according to any one of claims 1 to 9 wherein the liquid includes a prepolymer component having a straight chain (e.g. non-branched) structure.

11. A method according to any one of claims 1 to 10 wherein absorbance of a sample of a material is defined as A_λ :

$$A_\lambda = \log_{10} \left(\frac{I_0}{I} \right)$$

where I_0 is the light intensity before entering the sample and I is the intensity of light that is transmitted by the sample, and the proportion of the incident light absorbed by the sample is proportional to its thickness L ,

20 and wherein:

for the bulk material of the particles, A_λ/L is not more than 0.1/cm; and/or

for the bulk material of the matrix, A_λ/L is not more than 0.1/cm.

12. A method according to any one of claims 1 to 11 wherein, for each region to be treated with the electric field, the electric field is applied for not more than 100 ms.

13. A composite material having a periodic arrangement of particles distributed in a matrix, the refractive index of the material of the particles being different to the refractive index of the material of the matrix and the periodicity being such that, when illuminated

with white light, the periodic arrangement provides structural colour, wherein the periodic arrangement of the particles is formed (or is capable of being formed) by applying an electric field across a distribution of the particles in a curable liquid and the matrix is formed by curing the curable liquid to thereby fix the periodic arrangement of the particles.

5

14. A composite material according to claim 13 provided as a component in sheet or film form, or in filament or fibre form.

10

15. A composite material according to claim 14 wherein the component has substantially uniform thickness.

15

16. A composite material according to any one of claims 13 to 15 wherein one or more regions treated with the electric field form coloured regions and the remainder of the sheet provides a substantially white background.

17. Use of a composite material according to any one of claims 13 to 16 to display a structured colour arrangement.

18. A structural colour printing system having a printer head with electric field application means, the system further having an irradiation source, wherein the system is adapted to form a localised fixed periodic arrangement of particles distributed in a matrix by:

applying an electric field across a distribution of the particles in a curable liquid using the electric field application means; and
25 applying curing radiation to the curable liquid by operation of the irradiation source to form the matrix, thereby fixing the periodic arrangement of the particles.

19. A system according to claim 18 adapted to apply the electric field at a localised region, thereby forming only a localised region of the periodic arrangement of particles in the liquid, adjacent a region of randomly dispersed particles in the liquid.
- 5 20. A system according to claim 18 or claim 19 wherein the irradiation source is provided as part of the printer head.

1/4

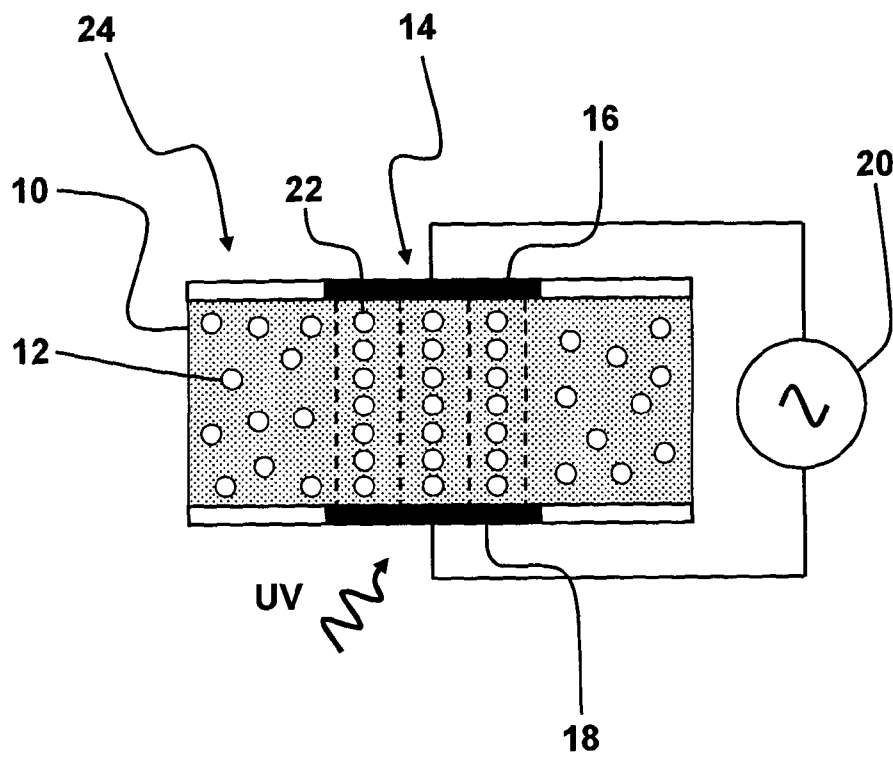


Fig. 1

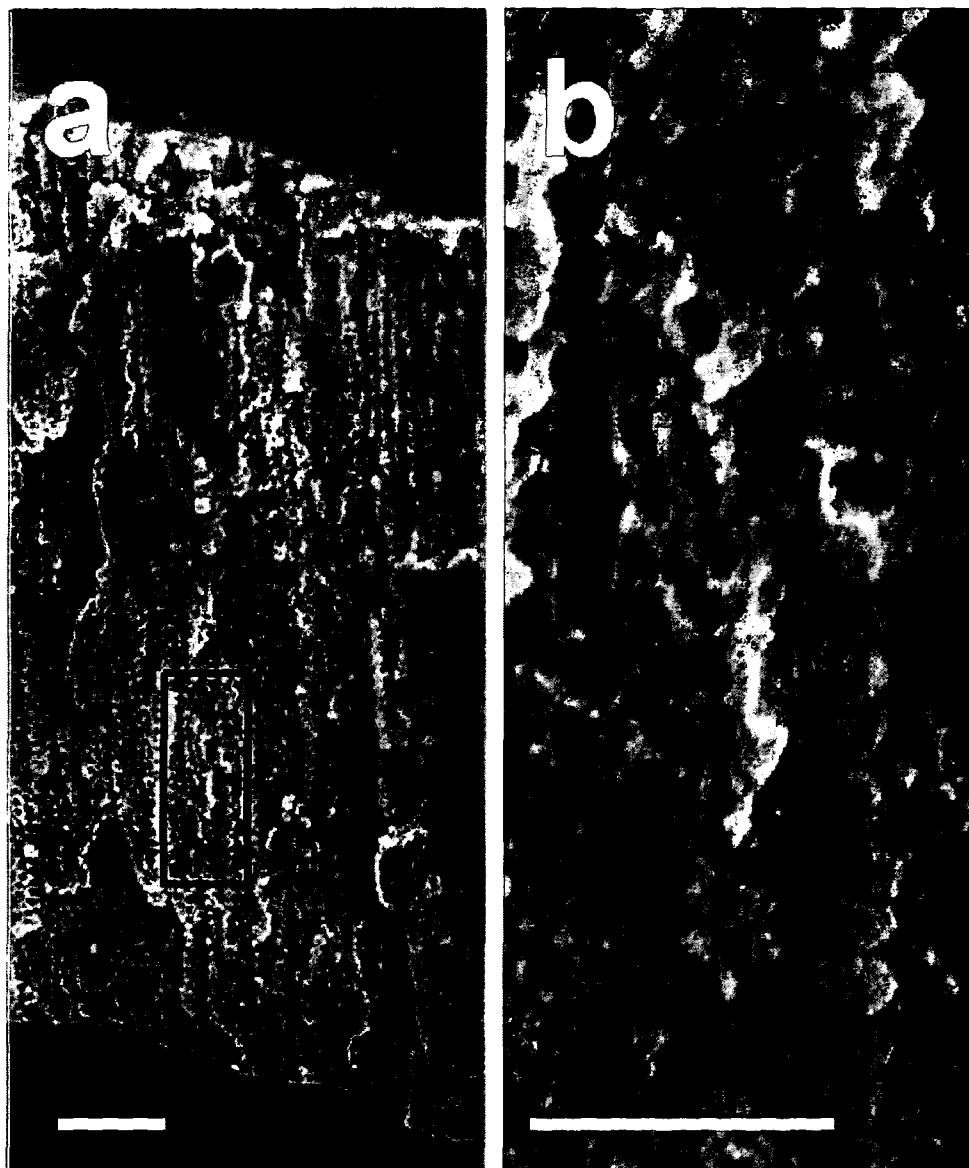
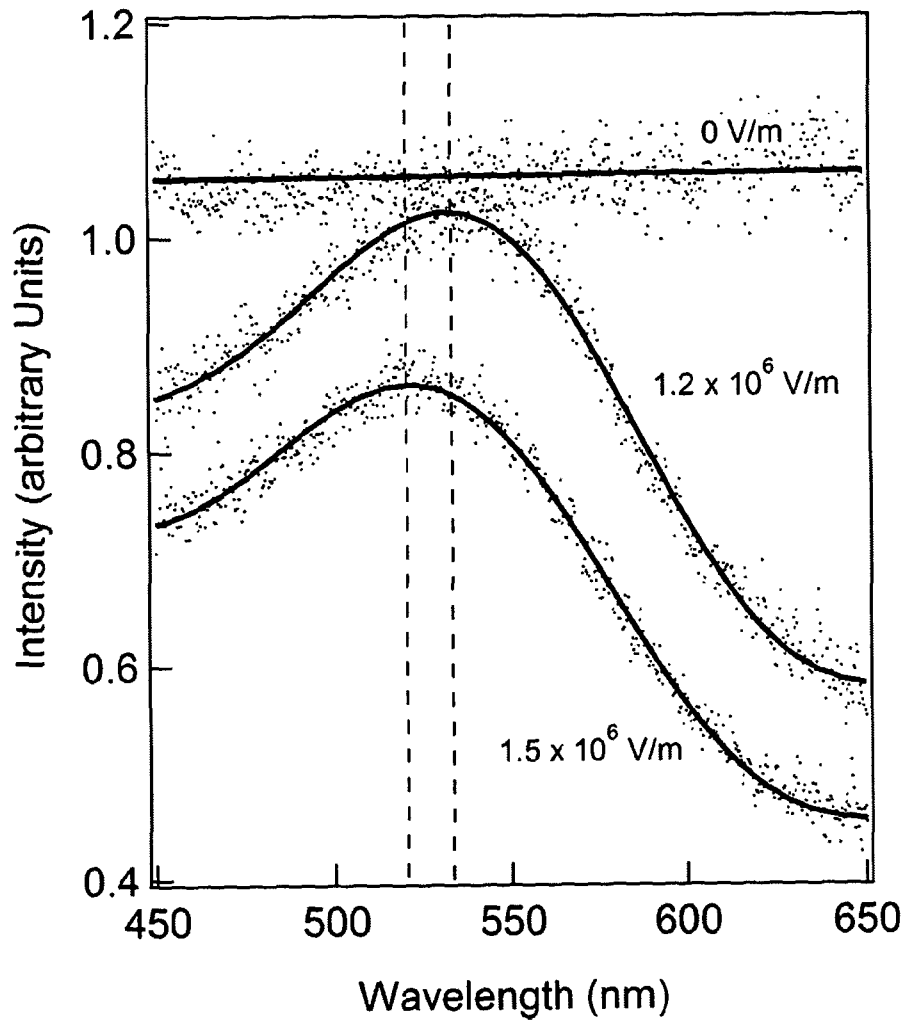


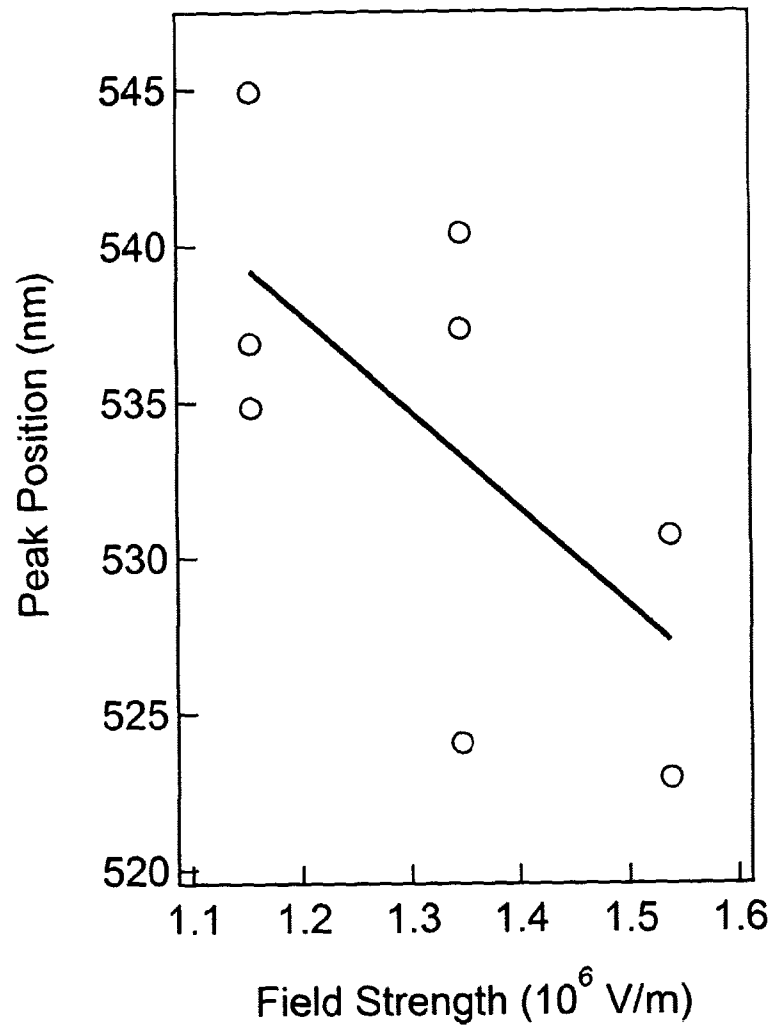
Fig. 2a

Fig. 2b

3/4

**Fig. 3**

4/4

**Fig. 4**

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/000278

A. CLASSIFICATION OF SUBJECT MATTER

INV. G02B1/00

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)

G02B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/120361 A2 (UNIV CALIFORNIA [US]; KWON SUNGHOON [KR]; YIN YADONG [US]; GE JIANPING) 21 October 2010 (2010-10-21) abstract paragraph [0004] - paragraph [0010] paragraph [0078] figures	1-20
A	----- WO 2008/100901 A1 (MASSACHUSETTS INST TECHNOLOGY [US]; BOYCE MARY C [US]; MULLIN TOM [GB]) 21 August 2008 (2008-08-21) abstract page 4 - page 6, line 3 figures	1-20
A	----- US 2010/046572 A1 (DE ROSSI ALFREDO [FR] ET AL) 25 February 2010 (2010-02-25) abstract; figures ----- -/-	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

24 July 2012

Date of mailing of the international search report

31/07/2012

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European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Seibert, Joachim

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/000278

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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