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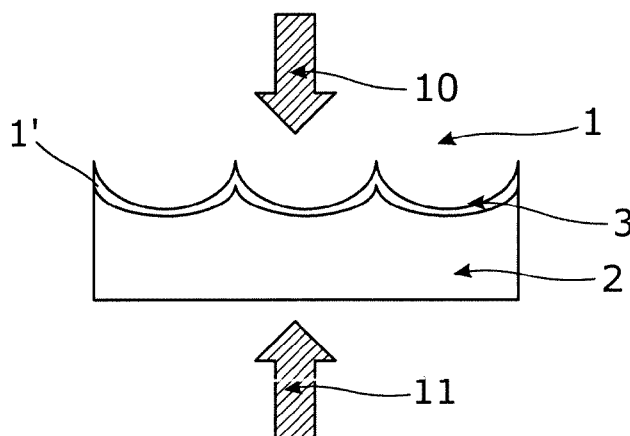


Figure 1a

(57) Abstract: The present invention relates to a textured metallic surface and a layer of material comprising said textured metallic surface, methods of manufacture and uses thereof.



TEXTURED SURFACES

Field of the Invention

- 5 The present invention relates to a textured surface and a layer of material comprising said textured surface, methods of manufacture and uses thereof. The present invention also relates to articles comprising the textured surface and layer of material and the use of said textured surface and layer of material in various applications including in displays, anti-counterfeiting and/or security applications and generally as an opacifier.
- 10 In addition, the present invention also relates to methods of modifying the appearance of metallic surfaces, for example by providing white or black metallic surfaces.

Background of the Invention

- 15 The appearance of a surface may be modified in numerous ways. For example, in order to modify the appearance of a surface so that it appears white, it is necessary for the surface to scatter light away without loss (i.e. with no, or minimal, absorption of light), over as wide a range of angles as possible. A white coating, such as paint or ink, achieves this via the use of non-absorbing high-refractive index particles of random
- 20 size and distribution, producing a scattering medium. This approach generally works well, but it may be necessary to take the opacity of the paint or ink into account and use a thick coating of paint or ink if it is desirable to have an opaque coating, such that, for example, no, or minimal light, is transmitted through the coating. Transmission of light will degrade the 'whiteness' of the coated surface. It has hitherto proved difficult,
- 25 *inter alia* to provide thin structures which are of a good quality white without having to resort to the use of relatively thick coating layers (typically at least tens of microns in thickness for a white paint).

- There is a need for thin white structures which are suitable for use in a range of
- 30 applications, for example in document manufacture and in various other applications including in displays. Providing thin structures which are white in appearance has, up until the present invention, proven difficult and, as such, there is an on-going need for surfaces, or thin structures, which possess a highly reflective diffuse white appearance when viewed under visible band optical illumination. Thin structures for the purposes
- 35 of the present application are generally taken to mean structures which are about 10nm to about 10mm in thickness, for example less than about 50µm in thickness.

More generally, it has been recognised that it would be advantageous to be able to modify the appearance of surfaces, particularly metallic surfaces, without necessarily compromising the essential metallic nature of that surface, other than in connection with the appearance and optical properties thereof, and without having to resort to the use of unduly thick coatings. Such modified metallic surfaces would be of use in a broad range of applications.

The use of textured surfaces to produce optical effects which can be used in security devices and markings and/or anti-counterfeiting tags and markings is known. For example, it is known to use textured surfaces to produce optical multilayers. However, the white, or indeed black, visual appearance of the surface produced in accordance with the present invention provides, *inter alia*, for a new "colour" component in such applications including those applications relating to holography.

Summary of the Invention

The present invention is based on the surprising finding that by providing a metalized thin textured surface then, rather than a metallic or silver appearance, a highly reflective white appearance results when viewed under visible band optical illumination. In embodiments of the invention a highly absorbing black appearance may also be provided.

The textured surface comprises optical microstructures. The optical microstructures may be arranged in a regular array. For example, the optical microstructures may be arranged in a regular hexagonal array. The optical microstructures may comprise pits or dimples so that the surfaces of the layers comprise a plurality or array of pits, dimples, bowls, indentations, depressions or wells - any of which may be arranged in a regular array. The optical microstructures may be arranged so that adjacent optical microstructures are touching, or tessellate, or overlap, and therefore the amount of (flat) surface between the optical microstructures is minimised. For example, up to about 100% of the textured surface may be accounted for by optical microstructures, for example about 90% to about 100%. Selected areas of the surface may, optionally, be left devoid of optical microstructures in order to tailor the appearance of the surface for identification purposes. In addition to the optical microstructures, the textured surface comprises surface relief features. The textured surface may be rough or roughened.

Accordingly, in a first aspect, the present invention provides a layer of material comprising at least one textured metallic surface, wherein the textured metallic surface comprises optical microstructures. For convenience, the layer of material in accordance with the present invention may be referred to herein as the structured material.

The metallic surface comprises at least one metal or metal containing compound. Alternatively, the metallic surface may consist of or consist essentially of a metal or metal containing compound. The present inventors have found that silver or silver containing compounds are particularly useful for providing a bright white highly reflective surface and, in certain embodiments, a black surface.

The textured metallic surface possesses, comprises, or has formed thereon, surface relief features, i.e. the textured metallic surface may be rough or roughened. The surface relief features may be present on a part of the textured metallic surface or they may be present across substantially the whole of the textured metallic surface or they may be present across the whole of the textured metallic surface. For example, at least about 30%, or at least about 50%, or at least about 95% of the textured surface may be rough and optionally up to about 100% may be rough. The surface relief features may possess a range of dimensions comprising or containing features in the range of about 100nm to about 9µm. Each optical microstructure may have a particular or unique set of surface relief features present thereon so that no two optical microstructures on the textured surface share precisely the same surface relief features.

The use of the textured surface and/or structured material in accordance with the present invention provides a number of beneficial features. For example, when viewing the structured material from the side on which the optical microstructures are present, the structured material provides a highly reflective white appearance at a wide range of viewing angles. The structured material may be at least about 60% reflecting. However, more typically the structured material may be up to about 80% reflecting. The reflectance is measured by illuminating the sample using a white light source, collecting the scattered light using an integrating sphere and measuring its spectral intensity using a spectrometer. The spectrum and reflectance are calibrated and normalised using a white reflectance standard (Labsphere SRS-99). Conversely, when viewing the structured material from the opposite side on which the optical

microstructures have been formed, the structured material may appear black. The opposite side of the structured material is typically smooth or non-rough when compared to the textured (and roughened) surface which comprises the optical microstructures.

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These visual effects provide for a broad range of applications for the structured material in accordance with the present invention, including, for example, in displays, anticounterfeiting and more generally as an effective opacifier, particularly when used in connection with thin structures. By thin structures is meant a structure which is typically about 10nm to about 10mm thick, for example about 50nm to about 1mm thick. The thin structures may be less than about 50 μ m thick.

The present invention also relates to methods for making the layer of material in accordance with the present invention. Accordingly, in a further aspect there is provided a method of making the layer of material in accordance with the invention, comprising forming optical microstructures on a substrate to provide a textured surface and depositing a metallic layer on to said textured surface to provide a textured metallic surface. The substrate may be a transparent or substantially transparent substrate. For example, the transparent substrate may be made from a transparent polymer. The use of a transparent substrate is particularly useful for providing a black surface. When the layer of material is viewed through the transparent substrate and in the direction of the surface of the layer of material which is opposite the textured surface, the appearance may be black.

Alternatively, a method of making the layer of material in accordance with the present invention comprises forming a series of optical microstructures in a metallic layer to form a textured surface.

Forming the optical microstructures on the surface of the substrate or in the metallic layer provides a textured surface comprising surface relief features or a rough or roughened surface in addition to the optical microstructures. A suitable technique for forming a series of optical microstructures and providing a roughened surface is laser drilling. An ultraviolet laser is a suitable type of laser.

The total number of optical microstructures present on a textured surface may be referred to herein as a series or an array of optical microstructures. A series or array of

optical microstructures may consist of or comprise at least about 10 optical microstructures or at least about 30 optical microstructures or typically covers an area of at least about $25\mu\text{m}^2$. The area which may be covered with optical microstructures is readily scaled upwards in size.

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In the various aspects of the invention, a further layer or layers may be deposited onto the textured metallic surface and/or onto the surface which is opposite and is substantially parallel to the textured metallic surface. These optional further layer or layers may be deposited onto the substrate onto which a metallic layer may have been deposited. These further layer or layers may comprise, either together in a single layer, or in separate layers, one or more of: a fluorescent material which may absorb ultraviolet light and emit at visible wavelengths further enhancing the brightness; a dielectric layer or multilayer, optionally comprising a pigment; a phosphorescent material; an electroluminescent material. The dielectric layer or multilayer may be used to cap the textured metallic surface.

The layer of material in accordance with the various aspects of the invention may be used in forming an article, product or device. Hence, according to a further aspect, there is provided an article, product or device comprising a layer of material in accordance with the present invention. The article, product or device may be a display device and, optionally, the layer of material may be present in said device performing the function of an electrode and/or a reflector. In particular, the layer of material may be present in a reflective display device, for example in electronic paper. Suitable examples of displays are electrophobic, electrowetting, electrophoretic and electrofluidic displays. The layer of material may also be used in an antenna or a frequency selective surface (FSS).

Accordingly, in a further aspect, there is provided the use of the layer of material in accordance with the present invention when used as (or as an) electrode and/or a reflector. There is also provided a display device (e.g. reflective display device) comprising said layer of material.

The layer of material in accordance with the invention is suitable for use in authenticating articles. As such, there is provided an article comprising the layer of material in accordance with the present invention wherein the article may take the form of a high value document or the packaging that surrounds an item of value. For

example, the article may be a banknote, cheque, credit card, identity card, medical card, ticket, legal document or deed or the article may be a label, casing or shrink-wrap. The banknote may be a polymer banknote. The layer of material in accordance with the invention may be incorporated as an insert, for example a polymer insert,
5 within a paper banknote or it could be used to form a polymer banknote.

The layer of material in accordance with the various aspects of the invention may be used for applications relating to anti-counterfeiting and/or security applications. Therefore, in a further aspect there is provided the use of a layer of material in
10 accordance with the invention for determining whether or not an article, comprising said layer of material, is genuine or counterfeit.

The use of the layer of material in accordance with the present invention provides a number of beneficial features. For example, the layer of material provides for easy and
15 straight-forward assessment of whether or not an article is genuine or counterfeit without necessarily requiring the use of additional equipment. The layer of material may readily be made visually appealing, or eye-catching, (for example, the layer of material may be easily patterned) which can be of importance if incorporated in an article which is to be used by the general public on a regular basis. The layer of
20 material may be used in connection with machine based identification. The layer of material may be used for the purposes of identification through the use of (distinctive) electrical, RF and optical characteristics. The layer of material in accordance with the present invention may be used to provide an aesthetic effect regardless of whether or not it is to be used in connection with anti-counterfeiting and/or security applications.
25 As such, and in accordance with a further aspect of the present invention, the use of a layer of material in accordance with the present invention to provide an aesthetic effect is provided. The layer of material in accordance with the present invention provides thin metallic structures which may be white or black in appearance and suitable for use in a range of display devices, particularly reflective display devices.

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Advantageously, the textured surface in accordance with the present invention exhibits large optical reflectivity across a range of wavelengths of light comprising the visible spectrum, whereby the optical reflectivity is diffuse in nature.

35 Any feature in one aspect of the invention may be applied to any other aspect or aspects of the invention, in any appropriate combination. In particular, product, device

or article aspects may be applied to method aspects, and vice versa.

Detailed Description of the Invention

5 Textured Surface

The textured metallic surface may be formed on a substrate and the structured material may comprise a metallic surface in contact with a substrate. Alternatively, the structured material may consist solely of a metallic layer which is textured. The
10 substrate may be a transparent substrate. The substrate may comprise or consist of a polymer. The polymer may be a homopolymer or a copolymer. Suitable examples of polymers are polycarbonate, cellophane, polypropylene, for example biaxially orientated polypropylene (BOPP). Commercial examples of suitable polycarbonates include Melinex which is available from DuPont Teijin Films, and Cellophane, which is
15 available from Innovia Films.

The texturing of the surface is provided by the presence of a plurality, series or array of optical microstructures. A textured surface may comprise at least about 10, for example at least about 30 or at least about 100 optical microstructures. The number of optical
20 microstructures is readily scalable to provide as many optical microstructures as may be required to cover a particular surface. For example, surfaces of at least $25\mu\text{m}^2$ and, by way of example, up to about $1\text{ or }2\text{m}^2$ may be covered. The textured surface may comprise or consist of optical microstructures of constant periodicity in a given direction. The optical microstructures may have a periodicity of about $1\mu\text{m}$ or greater
25 than about $1\mu\text{m}$, for example about $1\mu\text{m}$ to about $50\mu\text{m}$, for example about $3\mu\text{m}$ to about $20\mu\text{m}$ for example about $5\mu\text{m}$ to about $10\mu\text{m}$, typically about $9\mu\text{m}$. The periodicity is the distance between the centres of two adjacent optical microstructures. The periodicity may be approximately seven times the maximum wavelength of the incident light to be scattered (e.g. for visible light, about 5000nm). The optical
30 microstructures may be of the same size and/or shape. The optical microstructures may be identical in the absence of surface relief features. The optical microstructures may be arranged in an appropriate pattern, for example a hexagonal arrangement.

The optical microstructures may comprise pits or dimples so that the surfaces of the
35 layers comprise a plurality or array of pits, bowls, dimples, indentations, depressions or wells (any of which may be hemispherical), any of which may be arranged in a regular

array. The pits, bowls, dimples, indentations, concave depressions or wells may be circular in shape on viewing the textured surface from above. The optical microstructures may comprise an array of hemispherical dimples, or an array of pyramids, or an array of cones, or an array of truncated pyramids, or an array of truncated cones. The sides of the pyramids/truncated pyramids and the cones/truncated cones may be angled at about 45°. The optical microstructures may consist of or comprise a series of depressions in the textured surface in the form of channels or grooves. The channels or grooves may be rectangular or square or "V"-shaped or "U"-shaped in cross-section when viewed along the length thereof. The optical microstructures may be arranged so that adjacent microstructures are touching or nearly touching and therefore the amount of surface (e.g. flat surface) between the microstructures is minimised. For example, the amount of the flat surface between the optical microstructures may be less than about 10% of the total textured surface or substantially zero.

The size of the optical microstructures may be about 0.1µm or about 1µm to about 100µm, for example about 0.1µm or about 1µm to about 50µm or about 0.1µm or about 1µm to 10µm. For example, the width, or diameter, of the optical microstructures may be about 1µm to about 100µm, for example about 1µm to about 50µm or about 1µm to about 10µm. The width, or diameter, of the optical microstructures may be about 50µm to about 100µm. The depth of the optical microstructures may be about 0.1µm to about 100µm, for example about 0.1µm to about 50µm or about 0.1µm to about 10µm or about 0.1µm to about 5µm or from about 0.1µm to about 1.5µm. The size of the width (or diameter) and depth of the optical microstructure may be selected independently of each other. In an embodiment of the invention the optical microstructures may be about 8µm to about 10µm in width or diameter and about 0.5µm to about 5µm in depth. The dimensions of each of the optical microstructures may be independently selected. For each of the afore-mentioned ranges, in relation to the size of the optical microstructures, the lower end of the range may be about 1µm or about 2µm.

The textured surfaces may comprise optical microstructures wherein the microstructures are provided by a plurality of repeating three dimensional features, or irregularities, which are proud of the surface and arranged on a scale of about 0.5µm or about 1µm to about 100µm, independently, in width, depth and pitch, for example

about 0.5 μ m or about 1 μ m to about 50 μ m, or about 0.5 μ m or about 1 μ m to about 10 μ m. A suitable embodiment of such a feature comprises a plurality of pyramids.

The textured surface possesses surface relief features. The textured surface may be
5 rough or roughened. The surface relief features are typically present in an irregular arrangement. The surface relief features may possess a range of dimensions (e.g. length, breadth and height, independently selected from each other) comprising or containing features in the range of about 100nm or about 500nm to about 9 μ m or to about 1 μ m or about 2 μ m or about 3 μ m. The surface relief features may have a vertical
10 relief profile comprising a range of Fourier components corresponding to spatial wavelengths in the range of about 100nm to about 9000nm.

The surface relief features may be different or unique for each or substantially each of the optical microstructure on which they are present in order to provide particularly
15 effective scattering and minimise diffraction effects. In effect, this would mean that each or substantially each of the optical microstructures would be different by virtue of the surface relief features (or roughness) present on the optical microstructures.

The surface relief features may scatter light throughout the range of visible
20 wavelengths (approximately 380nm to 750nm) due to their range of dimensions, which span from sizes smaller than the shortest incident wavelength to greater than the longest incident wavelength. The random nature of the arrangements of the surface relief features prevents or minimises coloured diffraction effects from appearing in the angular distribution of the scattered light. The array of optical microstructures, each
25 preferably containing a unique arrangement of surface relief features, helps to average out any diffraction effects that may result from a limited range of features within any single optical microstructure. The shape or arrangement of the surface relief features may be different in or on each or substantially each of the optical microstructures. For example, any given surface relief features in a given optical microstructure may be
30 unique.

The textured surface is made from a metallic substance. Metals tend to provide high reflectivity, and, by way of example, silver has been found to provide the required effect and be particularly advantageous in surprisingly providing bright white surfaces and, in
35 some embodiments, black surfaces. The thickness of the metallic layer may be about 5nm to about 1mm, for example about 10nm to about 1000nm, for example about

100nm. The thickness of the metallic layer may be greater than the skin depth of the metal used, and preferably several times the skin depth to prevent optical transmission through the layer. The skin depth is the distance below the surface of the metal at which the electric field strength of incident radiation has diminished to $1/e$ (i.e. about 37%) of its value at the surface. For example, a thickness of about 100nm of silver has been shown to be sufficient for providing a bright white surface where the skin depth of silver is ~20 to 40nm at visible wavelengths. The metallic layer may be substantially conformal to the structured surface on which it is deposited (when used in combination with a substrate), and may be continuous or substantially continuous, i.e. there may be small areas of non-metal surface.

The present inventors have also observed that when the surface is formed by deposition of a metallic layer, e.g. a silver layer on a transparent substrate then the surface may appear white when viewing the textured layer and black when viewing from the opposite side of the textured layer and through the substrate.

As mentioned, the present inventors have found that silver works particularly well in the present invention and better than a number of other metals, for example, aluminium - the latter tending to provide a duller appearance. The reduced reflectivity of the other metals referred to may be attributed to optical loss due to absorption in the surface. Suitable metals for use in the present invention may have a permittivity that has a negative real part and a positive imaginary part. Silver has a permittivity of in the range $-2.75+i0.67$ to $-22.5+i1.40$ in the visible range of wavelengths (reference: Handbook of Optical Constants of Solids, Edward D. Palik, Academic Press, Boston, 1985).

Manufacture of the textured surface and the structured material

A textured surface in accordance with the present invention may be made by laser machining a suitable substrate through a (metal) mask containing an array of suitable holes or gaps and a suitable number thereof to transmit portions of a laser beam through to a substrate or directly onto a metal surface. The holes or gaps are of a suitable size, depending on the size of the optical microstructures (e.g. indentations or dimples) which are required. For example, the mask may comprise holes of about 500nm or $1\mu\text{m}$ to about 10mm or $100\mu\text{m}$ in diameter. The holes may be larger than the target size of the optical microstructures. The holes may also be arranged in a desired pitch, for example a regular repeating pattern. Laser drilling through the small hole in

the mask may produce an approximately hemispherical (or bowl shaped) dimple in the substrate or metal surface when the process is halted after the appropriate time, with the diameter of the dimples corresponding to the size of the holes in the mask or slightly smaller. The laser beam may be part of an optical system which may further
5 comprise an optical imaging system. There may also be present mechanical components for spatial translation of the substrate.

An example of a suitable laser is an ultraviolet laser, for example a pulsed excimer laser emitting ultraviolet radiation. The output of the laser may be directed to flood-
10 illuminate a metal mask. The optical system may also comprise an optical imaging system which may comprise a telescope for imaging the array of transmitted beams through the mask and onto the substrate with a suitable degree of magnification. Magnification may be used to produce smaller, or more focussed, beams at the substrate. The optical system may be adjusted to produce defocused beams at the
15 substrate.

The substrate comprises or consists of a suitable material. For example, the substrate may be a transparent polymer. The polymer may be a polycarbonate. Commercially available suitable samples include Melinex film. The thickness of the substrate may be
20 about 10 μ m to about 10mm, for example about 100 μ m to about 150 μ m. The laser may be directed at the substrate or metallic surface in suitable bursts (for example in the region of a few hundredths of a second up to about a tenth of a second) to machine the optical microstructures (e.g. "bowl" structures) with the desired surface relief features. Each burst of pulses may result in the machining of a number of optical
25 microstructures, for example thirty bowl structures, arranged in a sparse array determined by the geometry of the mask and the configuration of the optical system. A sparse array in this case indicates that a set of (e.g. 30) optical microstructures (e.g. bowls) is machined simultaneously such that they have a spacing of several times the final centre-to-centre bowl pitch. The mask may then be translated by one pitch and
30 the next set of bowls machined and interleaved with the first set. This process may be repeated until all of the space is filled with bowls. Between each burst of pulses, the sample may be translated, such that a regular arrangement of optical microstructures is formed, for example, a continuous close-packed hexagonal array of bowls may be produced with an area of 10 x 10mm.

For those embodiments of the invention which require a metallic layer to be deposited or coated on a substrate there are various suitable methods. Suitable methods include thermal evaporation. The substrate may be placed in a vacuum chamber, which may be evacuated to a suitable pressure, for example about 5×10^{-6} mbar. The metal to be deposited (e.g. silver) may be evaporated from a tungsten "boat" by electrically-induced heating, and depositing on the substrate at an appropriate rate, for example about 0.1 nm/s to an appropriate depth, for example about 100nm. The metallic layer may comprise or consist of a metal or metal containing compound. The metallic layer may be conformal or substantially conformal to the textured surface. The metallic layer may be continuous or substantially continuous.

Reproduction of the laser-machined surface may be performed by other means. For example, following production of the original surface by laser machining and prior to metal coating, a shim may be produced by electroforming in a hard metal such as nickel. Shims may be created that either have the same textured surface (or surface relief profile) as the original surface, or an inverted textured surface (or surface relief profile). The area of the textured surface may be increased at this stage by tiling of the surface to create multiple repeats of the original in an array. The nickel shims may then be used repeatably to create replicas of the original. For example, the shim with inverted features may be used to transfer the surface relief profile into a polymer substrate by embossing. Alternatively, an ultraviolet-curing epoxy may be deposited onto the shim and peeled off following curing. The embossing and deposition processes introduce a second inversion to the surface relief profile, thus reproducing the original. These polymer or epoxy substrates may then be coated with a suitable metal, e.g. silver to create a white metallic surface.

Uses of the textured surface

The structured material in accordance with the present invention may be used in applications relating to anti-counterfeiting and/or security. For example, the structured material may be incorporated into articles for use in brand protection and document security. The article may typically take the form of a high value document or the packaging that surrounds an item of value. For example, the article may be a banknote, cheque, credit card, identity card, medical card, ticket, legal document or deed or the article may be a label, casing or shrink-wrap. Small variations and tailored defects may be incorporated in the textured surface in order to introduce distinctive

optical effects similar to watermarking in traditional security paper. For instance, the omission of selected optical microstructures provides areas of high metallic reflectivity within the white surface. Such omissions may be arranged to produce distinctive markings, for example patterns, symbols or text. The process parameters in selected areas may be modified to be less white thereby introducing a feature similar to a traditional watermark. The introduction of single defects such as the omission of a single optical microstructure, or the formation of an array cell with modified roughness parameters, may be used, for example in connection with document identification or forensic validation.

The layer of material in accordance with the present invention is suitable for use in the manufacture of security holograms. The white visual appearance of the layer of material is suitable for providing a new 'colour' component in such holographic devices.

Functional properties of the present invention comprise the formation of white elements on the surface of a continuous metallic, conducting, film. Such a structure may be used as a white conducting electrode. Such an electrode is of use in a number of applications including thin film displays (especially reflective displays) and diagnostic testing.

The layer of material in accordance with the present invention has a high optical transmission loss. The layer of material may be employed where high optical reflectance is required but where transparency is undesirable. For example, the high reflectance surface is suitable for overcoating with traditional coloured inks without the need for a traditional 'undercoat' process. In effect, the structured material in accordance with the invention may be considered as a replacement for pigments such as titanium dioxide or kaolin or calcium carbonate which are used in traditional printable media such as paper.

Brief Description of the Figures

The invention will now be described, by way of example only and without limitation, with reference to the following Figures and Examples, in which:

Figure 1a is a cross-sectional view through a structured material in accordance with the invention.

Figure 1b is a more detailed view of one of the optical microstructures depicted in Figure 1a, illustrating the roughened surface.

Figure 1c is a cross-sectional view through a structured material in accordance with the invention wherein the optical microstructures are formed directly onto a metallic layer.

Figure 2 is a photograph of a white surface made in accordance with the present invention when viewed next to a coin which is metallic silver in appearance.

Figure 3 is an example of the surface topography of a white surface sample prepared in accordance with the present invention and as measured by atomic force microscopy (AFM).

Figure 4 illustrates examples of cross-sectional surface profiles taken from measured atomic force microscopy data for five different bowl depths.

Figure 5a is a representation of a reflective display device incorporating the structured material in accordance with the invention in an "off" or "white" state.

Figure 5b illustrates the device in Figure 5a when a voltage is applied and the device is in an "on" or "coloured" state.

Figure 1a illustrates a cross sectional view of a layer of material comprising a textured surface in accordance with the present invention, generally indicated by (1). In the embodiment shown, a metallic layer (1') has been deposited onto a substrate (2) which comprises an array of optical microstructures. The optical microstructures may be formed in the surface of the substrate (2) by laser drilling. An individual optical microstructure is labelled at (3). The presence of the optical microstructures provides a textured surface onto which the metallic layer (1') has been deposited. The metallic layer (1') conforms to the textured surface formed by the optical microstructures. In forming the optical microstructures, the textured surface is roughened.

This roughened surface is shown in greater detail in Figure 1b for a single microstructure. This enlarged view illustrates the surface relief features (4) in more detail. Preferably, all, or substantially all, of the textured surface will be roughened and the surface profile in each of the optical microstructures will be different. When the

metallic layer is deposited on the roughened surface it conforms to the roughened surface already present – this conformal metallic layer is shown in the exploded view of part of Figure 1b as feature 4(b).

5 The optical microstructures may be formed directly into a metallic layer to form a textured metallic surface. This is shown in simplified form in Figure 1c. The metallic layer is shown at (2c) and the optical microstructures (3c) are formed directly in said metallic layer (2c). An exploded view of the textured surface for one of the optical microstructures illustrating the surface relief features is shown at (4c).

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The substrate (2) may be made from a transparent material, for example a transparent polymer. When viewed from the direction indicated by the arrow (10) in Figure 1a the structured material is bright white in appearance. However, when viewed from the direction of (11), the appearance is black.

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Figure 2 is a photograph of a layer of material prepared in accordance with the invention when viewed in the general direction indicated by (10) in Figure 1a. For ease of comparison the metallic layer has only been deposited onto part of the substrate (2) so the contrast between the appearance of the uncoated and coated substrate can be appreciated. The coated areas are indicated at (12). Also, for comparison, a 20p coin (13) which is metallic silver in appearance is provided.

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Figure 3 shows the surface topography of a white surface sample prepared in accordance with the present invention and as measured by atomic force microscopy (AFM). The optical microstructures (bowls) and surface relief features (roughened surface) are clearly visible.

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Figures 5a and 5b are simplified representations of a reflective display device. Reflective displays use ambient light to illuminate the screen image and provide energy efficiency, sunlight legibility and are capable of being flexed or rolled. In electronic paper, high white state reflectance R (%) is critical; suitable examples include electrophobic, electrowetting, electrophoretic and electrofluidic displays.

30

Figure 5a shows a reflective display in the “white” state or the “off” state and Figure 5b shows the reflective display in the “on” or “coloured” state. The reflective display indicated generally at (20) comprises a substrate (21), e.g. a micromachined substrate

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comprising a reservoir (22) for storing ink (23). A channel or cavity (25) is defined by the space between two spaced electrodes, referred to herein as a front electrode (26) and rear electrode (27). In accordance with the invention, a white layer of material comprising a textured roughened surface forms the rear electrode (27) and provides the dual function of also acting as a high quality rear reflector. The front electrode (26) is transparent and may be made from indium tin oxide (ITO). The front electrode (26) is in contact with a protective substrate (28), e.g. a layer of glass or transparent plastic.

In the "off" or "white" state, incoming light (29) is simply reflected by the rear electrode (27) back through the front electrode (26) and substrate (28). In operation, and as indicated in Figure 5b, a voltage is applied between the electrodes (26, 27), causing the ink (23) to flow into the channel (25) between the two electrodes. Depending on the colour of the ink, the incoming light (29) will to some extent be absorbed and to some extent reflected. If the colour of the ink is black then most of the incident light will be absorbed and the display will appear black.

Examples

Example 1

A layer of material in accordance with the present invention was prepared as set out in the following procedure.

A sheet of pre-shrunk Melinex film of 140µm thickness was covered by a metal mask containing an array of 30 holes to produce optical microstructures of about 9µm in diameter. The output of a pulsed excimer laser emitting ultraviolet radiation was directed to flood-illuminate the metal mask. The laser was used in conjunction with an optical system which comprised a telescope that imaged the array of beams transmitted through the mask onto the substrate, with magnification such that the diameter of each focused beam was approximately 9µm. Bursts of laser pulses were directed at the substrate to machine the "bowl" structures with the desired surface relief features. Each burst of pulses resulted in the machining of thirty bowl structures, arranged in a sparse array determined by the geometry of the mask. Between each burst of pulses, the sample was translated, such that a continuous close-packed hexagonal array of bowls was produced with an area of 10 x 10mm.

In order to produce the white metallic surface, the laser-machined substrate surface was coated with silver by thermal evaporation. The substrate was placed in a vacuum chamber, which was evacuated to a pressure of 5×10^{-6} mbar. Silver was evaporated from a tungsten “boat” by electrically-induced heating, and deposited on the substrate
5 at a rate of 0.1 nm/s to a depth of 100nm.

In Figure 2, the appearance of the white surface (12) obtained is compared with a coin (13) which is metallic silver in appearance and with the surface of the uncoated substrate (2). It is evident that the appearance of the surface has been profoundly
10 modified. The small surface relief features scatter light throughout the range of visible wavelengths (approximately 380nm to 750nm) due to their range of dimensions which span from sizes which are smaller than the shortest incident wavelength to longer than the longest incident wavelength. The random nature of the arrangements of the surface relief features prevents or minimises coloured diffraction effects from appearing
15 in the angular distribution of the scattered light. The array of optical microstructures, each containing a unique arrangement of surface relief features, helps to average out any diffraction effects that may result from a limited range of features within any single optical microstructure.

20 Figure 3 illustrates the surface topography of the white surface sample prepared in accordance with the present invention and as measured by atomic force microscopy (AFM). It is clear from Figure 3 that substantially the entire surface has been roughened.

25 Examples of the bowl depth are in the range 0.5 μ m to 1.5 μ m. Examples of cross-sectional surface profiles taken from measured AFM data for five different bowl depths are shown in Figure 4.

Claims

1. A layer of material comprising at least one textured metallic surface, wherein the textured metallic surface comprises optical microstructures.
- 5 2. A layer of material according to claim 1 wherein the textured metallic surface is roughened.
3. A layer of material according to claim 1 or 2, wherein the textured metallic surface
10 possesses surface relief features.
4. A layer of material according to any one of claims 1 to 3 wherein the textured metallic surface possesses surface relief features having a range of dimensions from about 100nm or about 500nm to about 9µm or to about 1µm or to about 2µm or to
15 about 3µm.
5. A layer of material according to claim 4, wherein the dimensions apply, independently, to the length, breadth and height of said surface relief features.
- 20 6. A layer according to any one of claims 1 to 5, wherein the textured metallic surface has a vertical relief profile comprising a range of Fourier components corresponding to spatial wavelengths in the range of about 100nm to about 9000nm.
7. A layer of material according to any one of claims 1 to 6, wherein the layer of
25 material comprises a metallic layer deposited on a substrate.
8. A layer of material according to claim 7, wherein the substrate is a transparent substrate, for example a transparent polymer substrate.
- 30 9. A layer of material according to claim 7 or 8, wherein the substrate is a polycarbonate substrate.
10. A layer of material according to any one of claims 7 to 9, wherein the substrate is about 10µm to about 10mm thick, for example about 100µm to about 150µm thick.

11. A layer of material according to any one of claims 1 to 6, wherein the layer of material consists solely of the textured metallic surface.
12. A layer of material according to any one of claims 1 to 11, wherein the layer of material, or textured metallic surface, consists of, consists essentially of, or comprises silver or a silver containing material.
13. A layer of material according to any one of claims 1 to 12, wherein the optical microstructures have a periodicity of about $1\mu\text{m}$ or greater than about $1\mu\text{m}$, for example about $1\mu\text{m}$ to about $50\mu\text{m}$, for example about $3\mu\text{m}$ to $20\mu\text{m}$ for example about $5\mu\text{m}$ to about $10\mu\text{m}$, for example about $9\mu\text{m}$.
14. A layer of material according to any one of claims 1 to 13, wherein the optical microstructures are arranged in a regular hexagonal array.
15. A layer of material according to any one of claims 1 to 14, wherein the optical microstructures consist of or comprise pits, bowls or dimples.
16. A layer of material according to any one of claims 1 to 15, wherein the size of the optical microstructures is about $0.1\mu\text{m}$ or about $1\mu\text{m}$ to about $100\mu\text{m}$, for example about $0.1\mu\text{m}$ or about $1\mu\text{m}$ to about $50\mu\text{m}$ or about $0.1\mu\text{m}$ to about $10\mu\text{m}$.
17. A layer of material according to any one of claims 1 to 16, wherein the depth of the optical microstructures is about $0.1\mu\text{m}$ to about $100\mu\text{m}$, for example about $0.1\mu\text{m}$ to about $50\mu\text{m}$ or about $0.1\mu\text{m}$ to about $10\mu\text{m}$ or about $0.1\mu\text{m}$ to about $5\mu\text{m}$ or from about $0.1\mu\text{m}$ to about $1.5\mu\text{m}$.
18. A layer of material according to any one of claims 1 to 17, wherein the thickness of the textured metallic surface may be about 5nm to about 1mm , for example about 10nm to about 1000nm , for example about 100nm .
19. A method of making the layer of material according to any one of claims 1 to 10 or 12 to 18, comprising forming optical microstructures on a substrate to provide a textured surface and depositing a metallic layer on to said textured surface to provide a textured metallic surface.

20. A method of making the layer of material according to any one of claims 1 to 6 or 11 to 18, comprising forming a series of optical microstructures in a metallic layer to form a textured surface.
- 5 21. A method according to claim 19 or 20, wherein the optical microstructures are formed by a laser, for example an ultraviolet laser.
22. A method according to any one of claims 19 to 21, wherein one or more layers are further deposited onto the textured metallic surface.
- 10 23. An article, product or device comprising the layer of material according to any one of claims 1 to 18.
24. An article, product or device according to claim 23, wherein the device is a
15 display device, for example a reflecting display device.
25. A display device according to claim 24, wherein the display device is an electrophobic , electrowetting, electrofluidic or electrophoretic device.
- 20 26. A display device according to claim 24 or 25, wherein the layer of material is present as an electrode and reflector.
27. An article, product or device according to claim 23, wherein the article is a banknote, cheque, credit card, identity card, medical card, ticket, legal document or
25 deed or the article may be a label, casing or shrink-wrap.
28. An article according to claim 23, wherein the article is a banknote, for example a polymer banknote or a paper banknote.
- 30 29. The use of a layer of material in accordance with any one of claims 1 to 18, for determining whether or not an article, comprising said layer of material, is genuine or counterfeit.
- 35 30. The use of a layer of material in accordance with any one of claims 1 to 18, for providing an aesthetic effect.

31. The use of a layer of material in accordance with any one of claims 1 to 18 as an electrode and/or a reflector.

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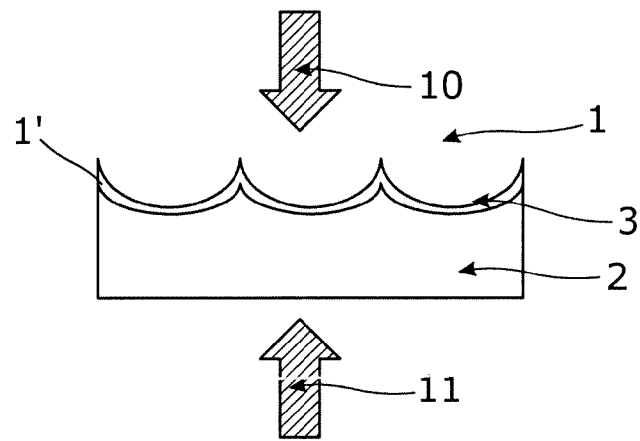


Figure 1a

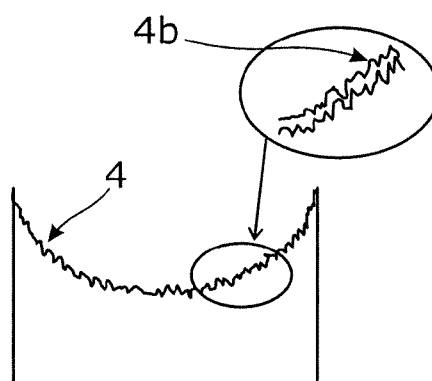


Figure 1b

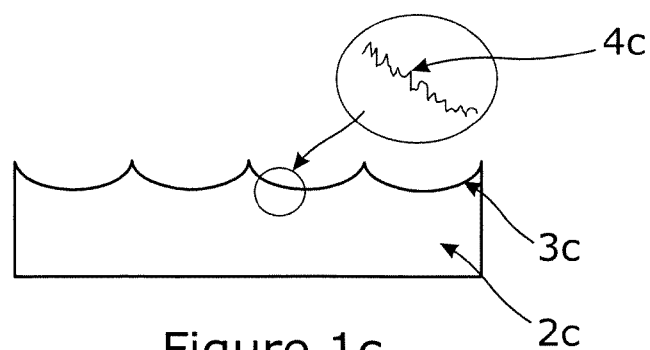


Figure 1c

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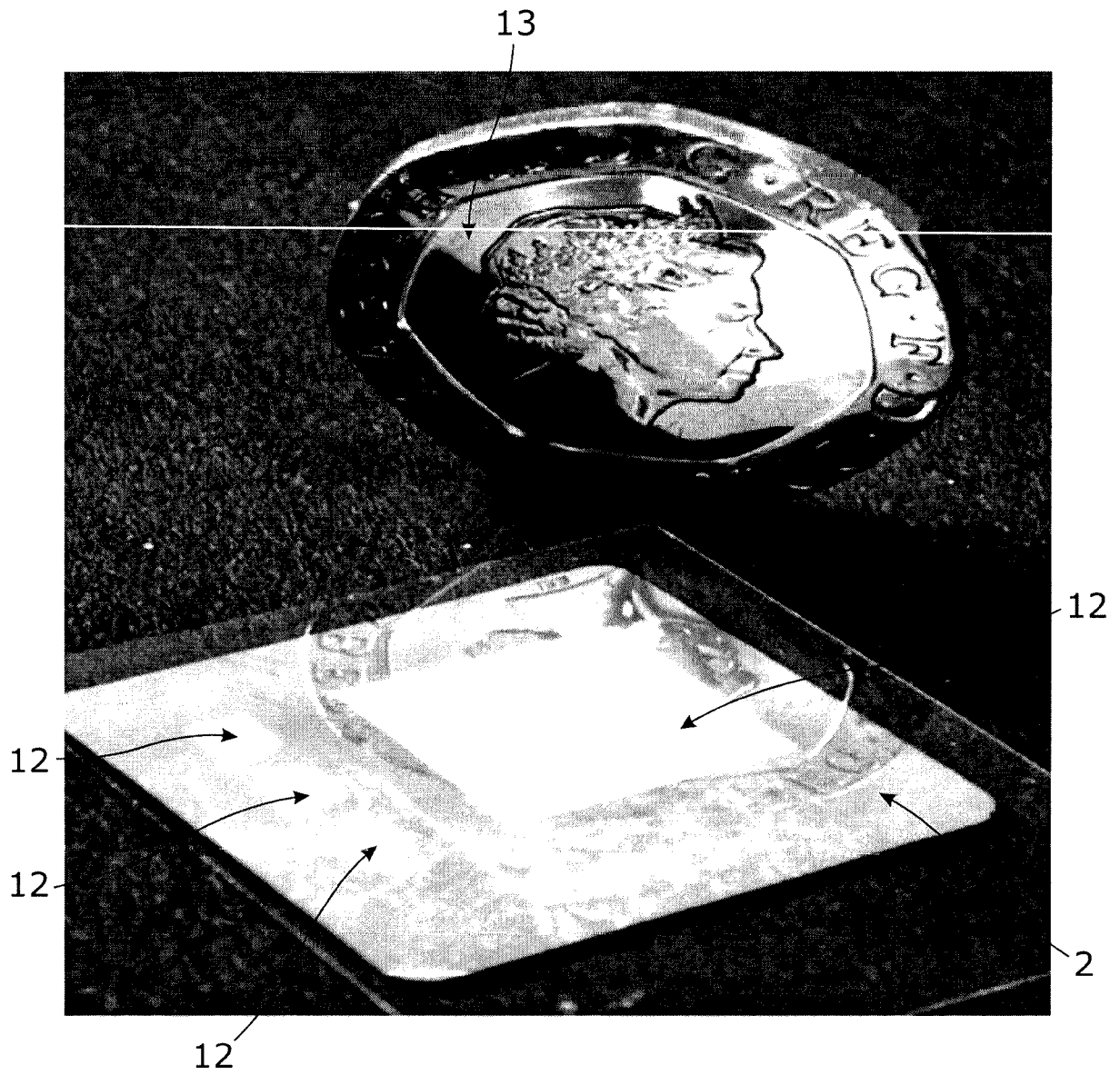


Figure 2

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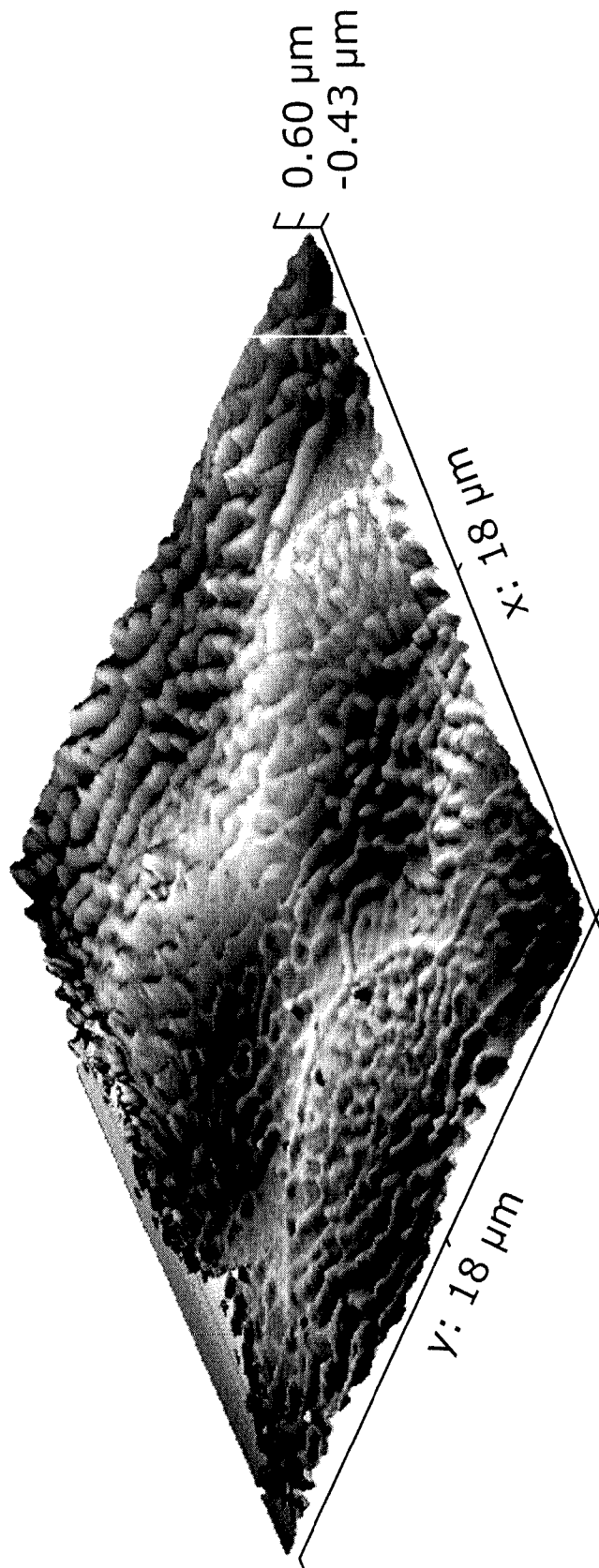


Figure 3

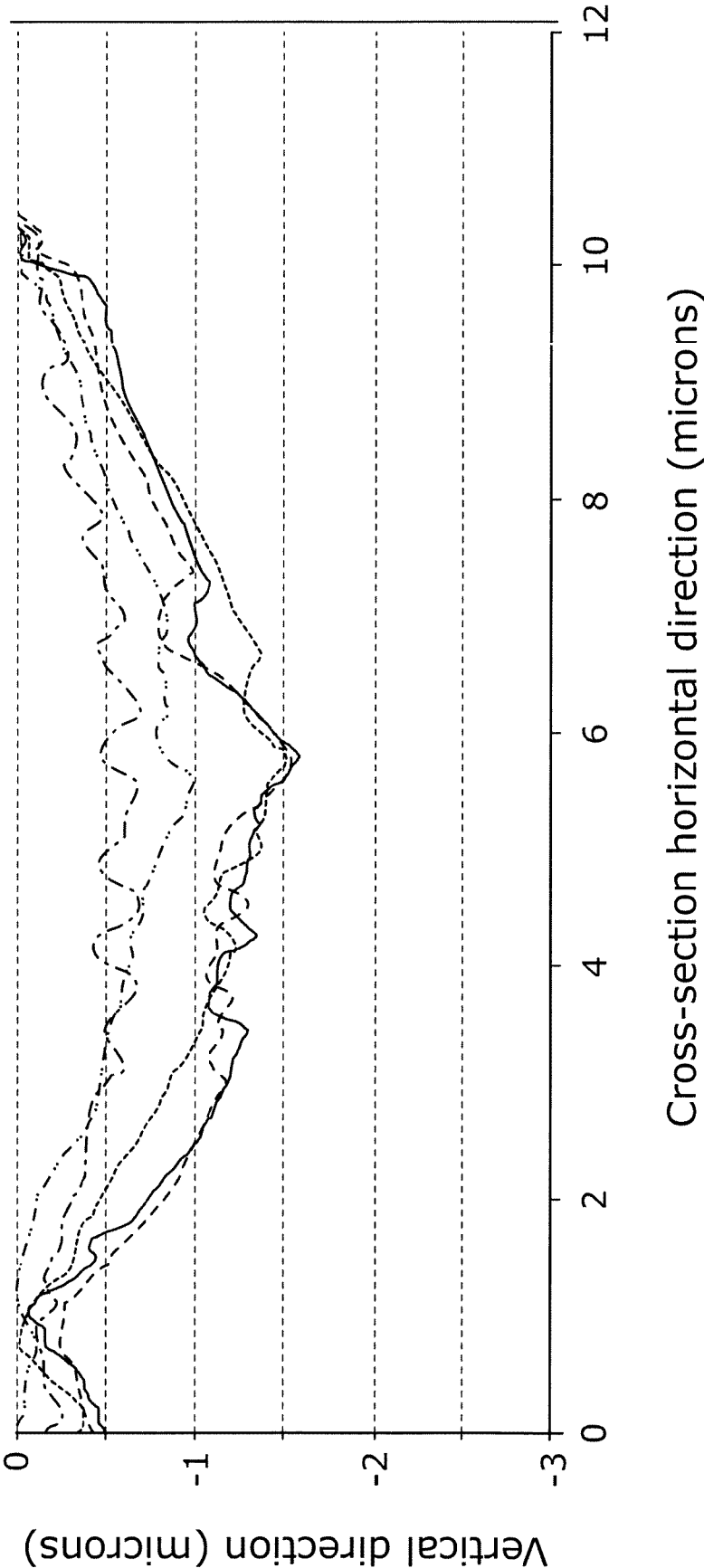


Figure 4

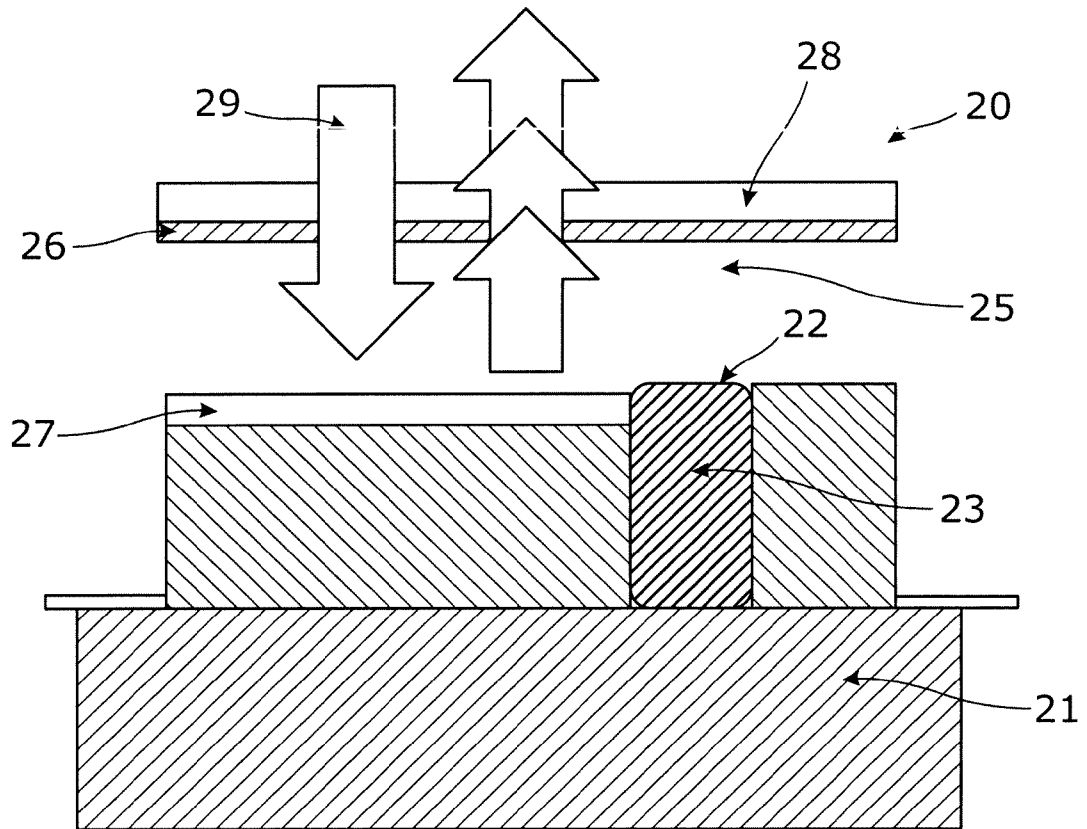


Figure 5a

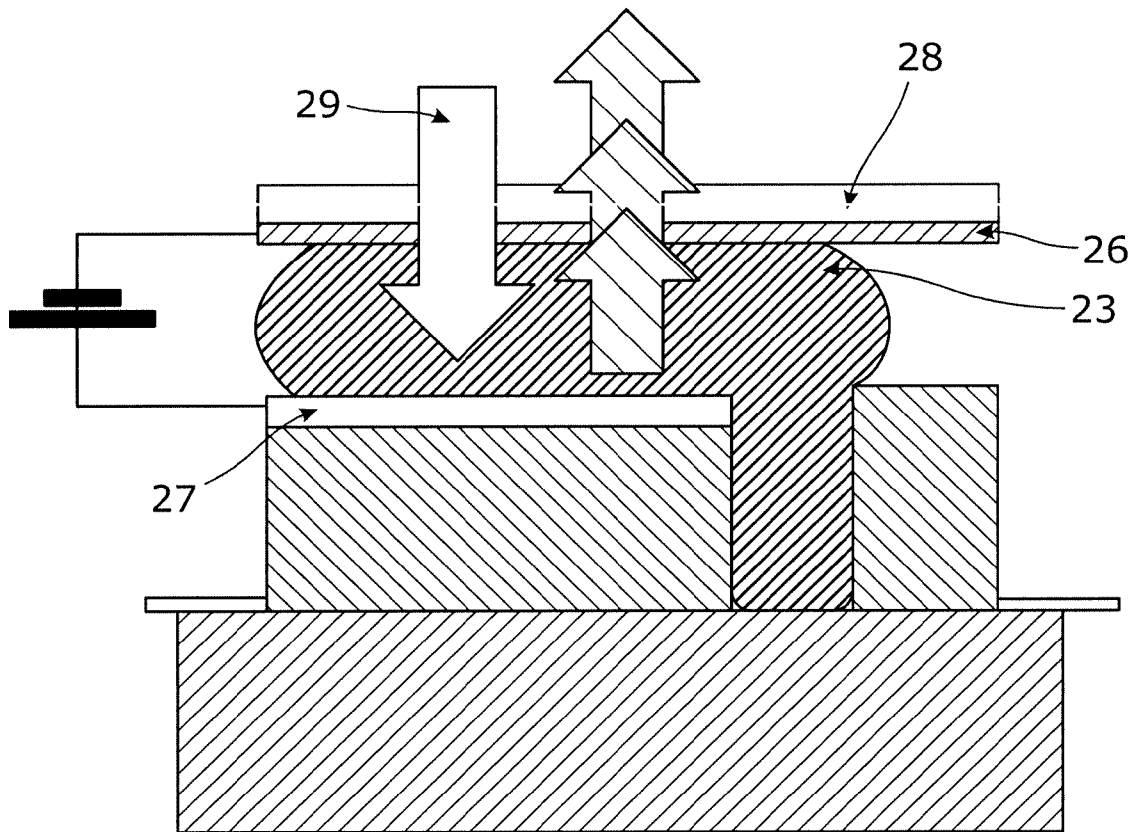


Figure 5b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062796

A. CLASSIFICATION OF SUBJECT MATTER

INV. B44C1/14 B42D15/10 G02F1/1335
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)

B44C B42D 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 2011/156038 A1 (YANG CHING-JUNG [TW] ET AL) 30 June 2011 (2011-06-30) paragraph [0039]; figure 1 -----	1,19,24, 26,31
X	US 2008/151158 A1 (KOITO TAKEO [JP] ET AL) 26 June 2008 (2008-06-26) paragraph [0056]; figure 5B -----	1,19,24, 26,31
X	US 2007/188683 A1 (NAKA KENICHIROU [JP]) 16 August 2007 (2007-08-16) paragraph [0048]; figure 1 ----- -/-	1,19,24, 26,31



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

5 September 2013

Date of mailing of the international search report

16/09/2013

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Attalla, Giancarlo

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/062796

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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Information on patent family members

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