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(54) Title: INTERLAYER FORMULATION FOR FLAT FILMS

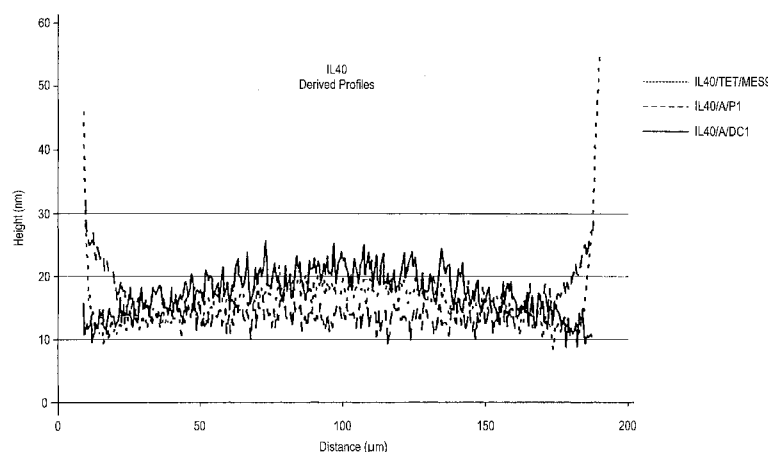


Fig. 4

(57) **Abstract:** A composition suitable for printing of an opto-electrical device, comprises a semiconducting hole transport material, a first solvent and a second solvent, the first solvent being 1-tetralone, benzylbenzoate and 1-methoxynaphthalene o-xylene, mixed-xylene, ethylbenzene, propylbenzene, butylbenzene having a higher boiling point and a greater viscosity than the second solvent, the second solvent being mesitylene, o-xylene, mixed-xylene, ethylbenzene, propylbenzene, butylbenzene. The solvents are miscible with one another and the viscosity of the first solvent is in the range of 5 to 12 mPas. The first solvent has a boiling point between 250 and 350 °C, and the second solvent has a boiling point between 100 and 200 °C. The figure shows derived interlayer film profiles when printed onto PEDOT (PD239). The old formulation shows edge thickening whereas two new formulations give slight edge thinning.

## INTERLAYER FORMULATION FOR FLAT FILMS

The present invention is concerned with a composition containing a hole transport material or hole injection material, or light-emitting polymer material, electron transport material or electron injection layer material, said composition being suitable for deposition by ink jet printing nozzle coating, spray coating, roll printing, dip coating, slot coating, flexographic printing in the manufacture of an organic light-emitting device.

### BACKGROUND TO THE INVENTION

A typical organic light-emitting device (OLED) comprises a substrate, on which is supported an anode, a cathode and a light-emitting layer situated in between the anode and cathode and comprising at least one polymeric electroluminescent material. In operation, holes are injected into the device through the anode and electrons are injected into the device through the cathode. The holes and electrons combine in the light-emitting layer to form an exciton which then undergoes radioactive decay to emit light.

Other layers may be present in the OLED, for example a layer of hole injection material, such as poly(ethylene dioxythiophene)/polystyrene sulphonate (PEDOT/PSS), may be provided between the anode and the light-emitting layer to assist injection of holes from the anode to the light-emitting layer. Further, a hole transport layer made from a hole transport material may be provided between the anode and the light-emitting layer to assist transport of holes to the light-emitting layer.

Luminescent conjugated polymers are an important class of materials that will be used in organic light emitting devices for the next generation of information technology based consumer products. The principle interest in the use of polymers, as opposed to inorganic semiconducting and organic dye materials, lies in the scope for low-cost device manufacturing, using solution-processing of film-forming materials. Since the last decade much effort has been devoted to the improvement of the emission efficiency of organic light emitting diodes

(OLEDs) either by developing highly efficient materials or efficient device structures.

A further advantage of conjugated polymers is that they may be readily formed by Suzuki or Yamamoto polymerisation. This enables a high degree of control over the regioregulatory of the resultant polymer.

Conjugated polymers may be solution processable due to the presence of appropriate solubilising groups. Suitable solvents for polyarylenes, in particular polyfluorenes, include mono- or poly-alkylbenzenes such as toluene and xylene. Particularly preferred solution deposition techniques are spin-coating and inkjet printing.

Spin-coating is particularly suitable for devices wherein patterning of the electroluminescent material is unnecessary, for example for lighting applications or simple monochrome segmented displays.

Inkjet printing is particularly suitable for high information content displays, in particular full colour displays.

Other solution deposition techniques include dip-coating, roll printing and screen printing.

Inkjet printing of luminescent layers of OLEDs is described in, for example, EP 0880303. It is said that the luminescent layer is made from an organic compound. It is taught that a composition of an organic luminescent material suitable for ink jet printing needs to satisfy the conditions given on a numerical range for at least one of contact angle, viscosity and surface tension. The range given for contact angle is 30 to 170 degrees. The range given for viscosity is 1 to 20cp. The range given for surface tension is 20 to 70 dyne/cm. A preferred embodiment is said to be where the organic luminescent compound is a hole injection and transfer type material. A separate hole injection and transfer layer laminated to the luminescent layer also is disclosed. No particular limitation is imposed upon the forming method for such a hole injection and transfer layer, but it is said that it is possible to form the layer using the ink-jet method for example. Examples of materials constituting the hole injection and transfer layer are given as aromatic diamine based compounds such as TPD; MTDATA; quinacridone; bisstil anthracene

derivatives; PVK; phthalocyanine based complex such as copper phthalocyanine; porphin based compound; NPD; TAD; polyaniline; and the like.

In Example 2 of EP 0880303, a PVK hole injection layer is deposited on red and green luminescent layers by ink jet printing. The physical properties (viscosity, surface tension, contact angle) of the PVK are not provided. In Example 3 of EP 0880303, a hole injection layer material is mixed with the red, green and blue luminescent materials to form red, green and blue luminescent layers by using an ink-jet device.

WO 2006/123167 is concerned with compositions for ink jet printing conductive or semi-conductive organic material for use in manufacturing opto-electrical devices. It is said in WO 2006/123167 that a charge injecting layer may be deposited as a composition comprising a conductive organic material in a high boiling point solvent. PEDOT:PSS is exemplified as a conductive organic material. A method of forming a device by ink jet printing of a formulation comprising PEDOT (or possibly other hole injection materials) and a high boiling point solvent is disclosed.

WO 2006/123167 also discloses a composition comprising an organic electroluminescent material and a high boiling point solvent having a boiling point higher than water. There is no disclosure nor suggestion in WO 2006/123167 of depositing a semiconducting hole transport material by ink-jet printing to form a separate hole transport layer.

The key reasons for the interest in ink jet printing are scalability and adaptability. The former allows arbitrarily large sized substrates to be patterned and the latter should mean that there are negligible tooling costs associated with changing from one product to another since the image of dots printed on a substrate is defined by software. At first sight this would be similar to printing a graphic image – commercial print equipment is available that allows printing of arbitrary images on billboard sized substrates. However the significant difference between graphics printers and display panels is the former use substrates that are porous or use inks that are UV curable resulting in very little effect of the drying environment on film formation. In

comparison, the inks used in fabricating OLED displays are ink jet printed onto non-porous surfaces and the process of changing from a wet ink to dry film is dominated by the drying environment of the ink in the pixel. Since the printing process involves printing stripes (or swathes) of ink (corresponding to the ink jet head width) there is an inbuilt asymmetry in the drying environment. In addition OLED devices require the films to be uniform to nanometer tolerance. It follows that to achieve scalability and adaptability requires control of the film forming properties of the ink and a robustness of this process to changes in pixel dimensions and swathe timing.

However a key problem with ink jet printing is interlayer edge thickening in flat films. This is clearly seen in Figure 3. Such edge thickening results in edge thinning of the electroluminescent layer. Variation in the thickness of the electroluminescent film across a pixel leads to non-uniform emission and a decrease in device efficiency and lifetime.

There is a need therefore to provide formulations for ink jet printing which can produce flat edges or even thinner edge interlayers for flat film devices.

The present inventors have accordingly identified a need to provide further compositions suitable for deposition by ink-jet printing to achieve flat films and which overcome the above identified problems.

## SUMMARY OF THE INVENTION

Thus, a first aspect of the present invention provides a A composition suitable for ink-jet printing, nozzle coating, spray coating, roll printing, dip coating, slot coating, or flexographic printing of an opto-electrical device, which composition comprises a semiconducting hole transport material, hole injection material, light-emitting polymer material, electron transport material, or electron injection layer, a first solvent and a second solvent, the first solvent having a higher boiling point and a greater viscosity than the second solvent, wherein the solvents are miscible with one another and the viscosity of the first solvent is in the range of 5 to 12 mPas.

The first, higher viscosity, solvent is used to slow down the movement of a polymer towards the pixel edge during drying. The second solvent having a lower viscosity and a lower boiling point evaporates off leaving behind the more viscous first solvent.

Preferably, the composition has a total viscosity of less than 20 mPas. Preferably the viscosity of the first solvent is greater than 6 mPas. Even more preferably the viscosity of the first solvent is greater than 7mPa

The first solvent may be selected from any of 1-tetralone, benzylbenzoate and 1-methoxynaphthalene. Suitable solvents for the second solvent include mesitylene, o-xylene, mixed-xylene, ethylbenzene, propylbenzene, butylbenzene

The first solvent without being especially limited has a boiling point between 250 and 350°C. Typically the second solvent has a boiling point between 100 and 200°C.

The volume ratio of the first solvent to the second solvent is not especially limited and can include a 1:1 volume ratio.

Typically, a composition comprising a light-emitting material and a solvent has a solids content of around 1 w/v %. This range is imposed due to limitations of molecular weight of the emitter and viscosity of the composition, which needs to be within the viscosity threshold of the inkjet print head. The concentration of light-emitting material in an inkjet composition is typically maximised such that as much light-emitting material is deposited in each drop

of the composition. Even so, two or three passes of the inkjet head are generally necessary for a sufficient quantity of light-emitting material to be deposited to produce a light-emitting layer having a thickness of about 60 nm, which is the thickness required for optimal device performance. However, the present inventors have found that a hole transport layer may provide optimal performance at much lower thickness (around 10 nm). Hole transporting compositions may therefore be provided at much lower concentration.

A particular benefit of using such low concentrations is found in the case where the semiconducting hole transport material is a polymer in that much higher molecular weight semiconducting hole transport polymers may be used than the corresponding molecular weight of a light-emitting polymer. The semiconducting hole transport polymer may have a molecular weight in the range 40,000 to 400,000 Daltons. Such a semiconducting hole transport polymer preferably has a molecular weight of at least 350,000 Daltons (unless stated otherwise, polymer molecular weights provided herein are weights in Daltons relative to polystyrene measured by gel permeation chromatography). This is particularly beneficial if the polymer of the composition comprises crosslinkable groups because there is a higher number of crosslinkable groups per polymer chain in a higher molecular weight polymer.

Devices comprising light-emitting polymers with molecular weights of less than 250,000 Daltons suffer from poor device performance, and so light-emitting compositions suitable for inkjet printing are not formulated with such low molecular weight polymers. However, the present inventors have found that no such poor device performance is found for hole transporting polymers.

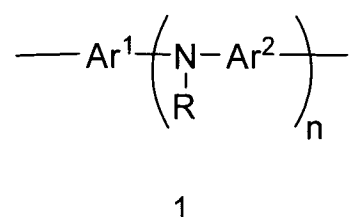
The jetting properties of the composition are strongly dependent on the solids content (the solids content of a composition may be determined simply by evaporating the solvent and weighing the remaining solid).

Typically, a composition containing a luminescent material for ink-jet printing will have a higher solids content of about 1 w/v%. Preferably the concentration of the semiconducting hole transport material in the composition is 0.8 w/v% or less.

In any of the compositions described herein, the semiconducting hole transport material may be cross linkable due to the presence of cross linkable groups.

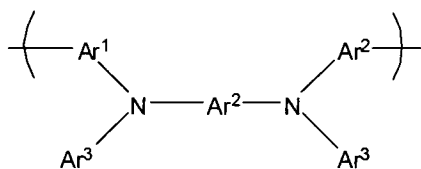
In any of the compositions described herein, the semiconducting hole transport material preferably comprises a polymer. Preferred semiconducting hole transport polymers comprise a triarylamine repeat unit.

Preferred triarylamine repeat units satisfy general Formula 1:

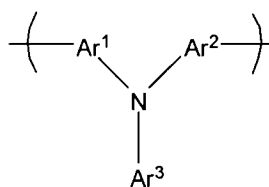


wherein Ar<sup>1</sup> and Ar<sup>2</sup> are optionally substituted aryl or heteroaryl groups, n is greater than or equal to 1, preferably 1 or 2, and R is H or a substituent, preferably a substituent. R is preferably alkyl or aryl or heteroaryl, most preferably aryl or heteroaryl. Any of the aryl or heteroaryl groups in the unit of formula 1 may be substituted. Preferred substituents include alkyl and alkoxy groups. Any of the aryl or heteroaryl groups in the repeat unit of Formula 1 may be linked by a direct bond or a divalent linking atom or group. Preferred divalent linking atoms and groups include O; S; substituted N; and substituted C.

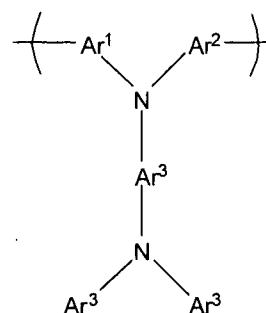
Particularly preferred units satisfying Formula 1 include units of Formulae 2-4:



2



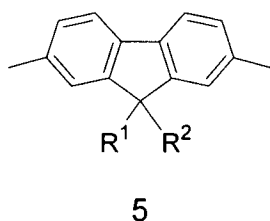
3



4

wherein  $Ar^1$  and  $Ar^2$  are as defined above; and  $Ar^3$  is optionally substituted aryl or heteroaryl. Where present, preferred substituents for  $Ar^3$  include alkyl and alkoxy groups.

Particularly preferred hole transporting polymers of this type are copolymers (particularly AB copolymers) of a triarylamine repeat unit and a second repeat unit. The second repeat unit preferably is a fluorene repeat unit, more preferably a repeat unit of Formula 5:



wherein  $R^1$  and  $R^2$  are independently selected from hydrogen or optionally substituted alkyl, alkoxy, aryl, arylalkyl, heteroaryl and heteroarylalkyl. More preferably, at least one of  $R^1$  and  $R^2$  comprises an optionally substituted  $C_4$ - $C_{20}$  alkyl or aryl group.

A second aspect of the present invention relation is a method of forming an organic light-emitting device including the steps of:

- a. providing an anode layer;
- b. optionally providing a conducting hole injecting layer on the anode layer;
- c. depositing a composition as defined herein on the anode or hole injecting layer by ink-jet printing to form a semiconducting hole transport layer, provided that when the semiconducting hole transport material is deposited by ink-jet printing then the semiconducting hole transport material is deposited on a hole injecting layer.

A third aspect of the present invention is a method of forming an organic light-emitting device including the step of:

1. depositing a composition as defined herein by ink-jet printing to form a semiconducting hole transport layer.

Preferably a method according to the second or third aspects of the invention includes a further step of baking the semiconducting hole transport layer by heating.

Baking conditions should be selected so that at least a part of the semiconducting hole transport layer is rendered insoluble so that the luminescent layer can be deposited without dissolving the semiconducting hole transport layer. This technique of baking the semiconducting hole transport layer is known in the art. A suitable temperature for baking is in the range of from 160 to 220 °C, preferably 180 to 200 °C.

In relation to the second and third aspects of the present invention, it will be understood that, typically, deposition of the defined composition will be onto an anode or a conducting hole injecting layer.

Preferably, in the methods according to the second and third aspects of the present invention, the thickness of the semiconducting hole transport layer is in the range from 5 to 40nm, more preferably 5 to 30 nm, more preferably from 8 to 20 nm, and most preferably about 10nm. The solvent can take anything between a few seconds and a few minutes to dry and results in a relatively thin film in comparison with the initial "ink" volume. Often multiple drops are deposited, preferably before drying begins, to provide sufficient thickness of dry material.

In all of the methods according to the second and third aspects of the present invention, the methods typically will include steps of depositing a luminescent layer on the semiconducting hole transport layer, optionally depositing an electron transport layer on the luminescent layer, and depositing a cathode on the luminescent layer or electron transport layer, where present.

It will be understood that in the second and third aspects of the present invention, preferably, the methods include a step of removing the solvent from the semiconducting hole transport layer after formation thereof. Preferred methods for removing the solvent(s) include vacuum drying at elevated temperature, typically up to 100°C depending on vacuum pressure. The provision of a high boiling point solvent increases the drying time of the composition.

In the methods according to the second and third aspects of the present invention, it will be appreciated that printing generally will be into a pixel defined by bank structures. In this connection, the desired viscosity of the composition will, to some extent, be dependent on the pixel size, drop diameter, drop volume, drop frequency, and wettability of the surface onto which the composition is being deposited. For small pixels a higher solids content is generally used. For larger pixels a lower solid content is used. For larger pixels, the concentration of the composition is reduced to get good film forming properties.

Preferably, the composition should have a contact angle with the bank such that it wets the base of the well but does not flood out of the well.

A fourth aspect of the present invention provides an organic light-emitting device made by a method according to the second or third aspects of the invention.

Preferred features of the device according to the fourth aspect of the present invention are provided below.

With reference to Figure 1, the architecture of an electroluminescent device according to the fourth aspect of the invention preferably comprises a (typically transparent glass or plastic) substrate 1, an anode 2 and a cathode 4. A luminescent layer 3 is provided between anode 2 and cathode 4.

In a practical device, at least one of the electrodes is semi-transparent in order that light may be emitted. Where the anode is transparent, it typically comprises indium tin oxide.

The semiconducting hole transport layer is present between anode 2 and luminescent layer 3. Further layers may be located between anode 2 and cathode 3, such as charge transporting, charge injecting or charge blocking layers.

In particular, it is desirable to provide a conductive hole injection layer, which may be formed from a conductive organic or inorganic material between the anode 2 and the semiconducting hole transport layer to assist hole injection from the anode into the semiconducting hole transport layer. Examples of doped organic hole injection materials include doped poly(ethylene

dioxythiophene) (PEDT), in particular PEDT doped with a charge-balancing polyacid such as polystyrene sulfonate (PSS) as disclosed in EP 0901176 and EP 0947123, polyacrylic acid or a fluorinated sulfonic acid, for example Nafion ®; polyaniline as disclosed in US 5723873 and US 5798170; and poly(thienothiophene). Examples of conductive inorganic materials include transition metal oxides such as VOx MoOx and RuOx as disclosed in Journal of Physics D: Applied Physics (1996), 29(11), 2750-2753.

The hole transporting layer located between anode 2 and luminescent layer 3 preferably has a HOMO level of less than or equal to 5.5 eV, more preferably around 4.8-5.5 eV. HOMO levels may be measured by cyclic voltammetry, for example.

If present, an electron transporting layer located between electroluminescent layer 3 and cathode 4 preferably has a LUMO level of around 3-3.5 eV.

A fifth aspect of the present invention provides a full colour display comprising an organic light-emitting device according to the fourth aspect of the invention.

A preferred full colour display comprises "red" pixels, "green" pixels and "blue" pixels, each pixel comprising an OLED as defined in relation to the fourth aspect. A "red" pixel will have a luminescent layer comprising a red electroluminescent material. A "green" pixel will have a luminescent layer comprising a green electroluminescent material. A "blue" pixel will have a luminescent layer comprising a blue electroluminescent material. Preferably, the hole transport layer is common to all colours.

By "red electroluminescent material" is meant an organic material that by electroluminescence emits radiation having a wavelength in the range of 600-750 nm, preferably 600-700 nm, more preferably 610-650 nm and most preferably having an emission peak around 650-660 nm.

By "green electroluminescent material" is meant an organic material that by electroluminescence emits radiation having a wavelength in the range of 510-580 nm, preferably 510-570 nm.

By "blue electroluminescent material" is meant an organic material that by electroluminescence emits radiation having a wavelength in the range of 400-500 nm, more preferably 430-500 nm.

Red, green and blue electroluminescent materials are known in the art.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The present invention now will be described in more detail with reference to the attached Figures, in which:

Figure 1 shows the architecture of a typical OLED; and

Figure 2 shows a vertical cross section through an example of an OLED.

Figure 3 shows edge thickening in an interlayer of a thin film.

Figures 4 to 6 show interlayer film profiles resulting from different solvent formulations.

#### DETAILED DESCRIPTION

Referring to the device according to the fourth aspect, luminescent layer 3 may consist of luminescent material alone or may comprise the luminescent material in combination with one or more further materials. In particular, the electroluminescent material may be blended with hole and/or electron transporting materials as disclosed in, for example, WO 99/48160, or may comprise a luminescent dopant in a semiconducting host matrix. Alternatively, the luminescent material may be covalently bound to a charge transporting material and/or host material.

Luminescent layer 3 may be patterned or unpatterned. A device comprising an unpatterned layer may be used as an illumination source, for example. A white light emitting device is particularly suitable for this purpose. A device comprising a patterned layer may be, for example, an active matrix display or a passive matrix display. In the case of an active matrix display, a patterned electroluminescent layer is typically used in combination with a patterned anode layer and an unpatterned cathode. In the case of a passive matrix display, the anode layer is formed of parallel stripes of anode material, and parallel stripes of electroluminescent material and cathode material arranged perpendicular to the anode material wherein the stripes of electroluminescent

material and cathode material are typically separated by stripes of insulating material ("cathode separators") formed by photolithography.

Suitable materials for use in luminescent layer 3 include small molecule, polymeric and dendrimeric materials, and compositions thereof. Suitable electroluminescent polymers for use in layer 3 include poly(arylene vinylenes) such as poly(p-phenylene vinylenes) and polyarylenes such as: polyfluorenes, particularly 2,7-linked 9,9 dialkyl polyfluorenes or 2,7-linked 9,9 diaryl polyfluorenes; polyspirofluorenes, particularly 2,7-linked poly-9,9-spirofluorene; polyindenofluorenes, particularly 2,7-linked polyindenofluorenes; polyphenylenes, particularly alkyl or alkoxy substituted poly-1,4-phenylene. Such polymers as disclosed in, for example, Adv. Mater. 2000 12(23) 1737-1750 and references therein. Suitable electroluminescent dendrimers for use in layer 3 include electroluminescent metal complexes bearing dendrimeric groups as disclosed in, for example, WO 02/066552.

Cathode 4 is selected from materials that have a workfunction allowing injection of electrons into the luminescent layer. Other factors influence the selection of the cathode such as the possibility of adverse interactions between the cathode and the electroluminescent material. The cathode may consist of a single material such as a layer of aluminium. Alternatively, it may comprise a plurality of metals, for example a bilayer of a low workfunction material and a high workfunction material such as calcium and aluminium as disclosed in WO 98/10621; elemental barium as disclosed in WO 98/57381, Appl. Phys. Lett. 2002, 81(4), 634 and WO 02/84759; or a thin layer of metal compound, in particular an oxide or fluoride of an alkali or alkali earth metal, to assist electron injection, for example lithium fluoride as disclosed in WO 00/48258; barium fluoride as disclosed in Appl. Phys. Lett. 2001, 79(5), 2001; and barium oxide. In order to provide efficient injection of electrons into the device, the cathode preferably has a workfunction of less than 3.5 eV, more preferably less than 3.2 eV, most preferably less than 3 eV. Work functions of metals can be found in, for example, Michaelson, J. Appl. Phys. 48(11), 4729, 1977.

The cathode may be opaque or transparent. Transparent cathodes are particularly advantageous for active matrix devices because emission through

a transparent anode in such devices is at least partially blocked by drive circuitry located underneath the emissive pixels. A transparent cathode will comprise a layer of an electron injecting material that is sufficiently thin to be transparent. Typically, the lateral conductivity of this layer will be low as a result of its thinness. In this case, the layer of electron injecting material is used in combination with a thicker layer of transparent conducting material such as indium tin oxide.

It will be appreciated that a transparent cathode device need not have a transparent anode (unless, of course, a fully transparent device is desired), and so the transparent anode used for bottom-emitting devices may be replaced or supplemented with a layer of reflective material such as a layer of aluminium. Examples of transparent cathode devices are disclosed in, for example, GB 2348316.

Optical devices tend to be sensitive to moisture and oxygen. Accordingly, the substrate preferably has good barrier properties for prevention of ingress of moisture and oxygen into the device. The substrate is commonly glass, however alternative substrates may be used, in particular where flexibility of the device is desirable. For example, the substrate may comprise a plastic as in US 6268695 which discloses a substrate of alternating plastic and barrier layers or a laminate of thin glass and plastic as disclosed in EP 0949850.

The device is preferably encapsulated with an encapsulant (not shown in Figure 1) to prevent ingress of moisture and oxygen. Suitable encapsulants include a sheet of glass, films having suitable barrier properties such as alternating stacks of polymer and dielectric as disclosed in, for example, WO 01/81649 or an airtight container as disclosed in, for example, WO 01/19142. A getter material for absorption of any atmospheric moisture and / or oxygen that may permeate through the substrate or encapsulant may be disposed between the substrate and the encapsulant.

#### Polymerisation methods

Preferred methods for preparation of semiconducting polymers are Suzuki polymerisation as described in, for example, WO 00/53656 and Yamamoto

polymerisation as described in, for example, T. Yamamoto, "Electrically Conducting And Thermally Stable  $\pi$  - Conjugated Poly(arylene)s Prepared by Organometallic Processes", Progress in Polymer Science 1993, 17, 1153-1205. These polymerisation techniques both operate via a "metal insertion" wherein the metal atom of a metal complex catalyst is inserted between an aryl group and a leaving group of a monomer. In the case of Yamamoto polymerisation, a nickel complex catalyst is used; in the case of Suzuki polymerisation, a palladium complex catalyst is used.

For example, in the synthesis of a linear polymer by Yamamoto polymerisation, a monomer having two reactive halogen groups is used. Similarly, according to the method of Suzuki polymerisation, at least one reactive group is a boron derivative group such as a boronic acid or boronic ester and the other reactive group is a halogen. Preferred halogens are chlorine, bromine and iodine, most preferably bromine.

It will therefore be appreciated that repeat units and end groups comprising aryl groups as illustrated throughout this application may be derived from a monomer carrying a suitable leaving group.

Suzuki polymerisation may be used to prepare regioregular, block and random copolymers. In particular, homopolymers or random copolymers may be prepared when one reactive group is a halogen and the other reactive group is a boron derivative group. Alternatively, block or regioregular, in particular AB, copolymers may be prepared when both reactive groups of a first monomer are boron and both reactive groups of a second monomer are halogen.

As alternatives to halides, other leaving groups capable of participating in metal insertion include groups include tosylate, mesylate and triflate.

#### Solution processing

A single polymer or a plurality of polymers may be deposited from solution to form layer 3. Suitable solvents for polyarylenes, in particular polyfluorenes, include mono- or poly-alkylbenzenes such as toluene and xylene. Particularly preferred solution deposition techniques are spin-coating and inkjet printing.

Spin-coating is particularly suitable for devices wherein patterning of the electroluminescent material is unnecessary – for example for lighting applications or simple monochrome segmented displays.

Inkjet printing is particularly suitable for high information content displays, in particular full colour displays. Inkjet printing of OLEDs is described in, for example, EP 0880303.

Other solution deposition techniques include dip-coating, roll printing and screen printing.

If multiple layers of the device are formed by solution processing then the skilled person will be aware of techniques to prevent intermixing of adjacent layers, for example by crosslinking of one layer before deposition of a subsequent layer or selection of materials for adjacent layers such that the material from which the first of these layers is formed is not soluble in the solvent used to deposit the second layer.

Organic LEDs may be deposited on a substrate in a matrix of pixels to form a single or multi-colour pixellated display. A multicoloured display may be constructed using groups of red, green, and blue emitting pixels. So-called active matrix displays have a memory element, typically a storage capacitor and a transistor, associated with each pixel whilst passive matrix displays have no such memory element and instead are repetitively scanned to give the impression of a steady image.

Figure 2 shows a vertical cross section through an example of an OLED device 100. In an active matrix display, part of the area of a pixel is occupied by associated drive circuitry (not shown in Figure 2). The structure of the device is somewhat simplified for the purposes of illustration.

The OLED 100 comprises a substrate 102, typically 0.7 mm or 1.1 mm glass but optionally clear plastic, on which an anode layer 106 has been deposited. The anode layer typically comprises around 150 nm thickness of ITO (indium tin oxide), over which is provided a metal contact layer, typically around 500nm of aluminium, sometimes referred to as anode metal. Glass substrates coated with ITO and contact metal may be purchased from Corning, USA.

The contact metal (and optionally the ITO) is patterned as desired so that it does not obscure the display, by a conventional process of photolithography followed by etching.

A substantially transparent conducting hole injection layer 108a is provided over the anode metal, followed by the semiconducting hole transport layer 108b and an electroluminescent layer 108c. Banks 112 may be formed on the substrate, for example from positive or negative photoresist material, to define wells 114 into which these active organic layers may be selectively deposited. The wells thus define light emitting areas or pixels of the display.

A cathode layer 110 is then applied by, say, physical vapour deposition. The cathode layer typically comprises a low work function metal such as calcium or barium covered with a thicker, capping layer of aluminium and optionally including an additional layer immediately adjacent the electroluminescent layer, such as a layer of lithium fluoride, for improved electron energy level matching. Mutual electrical isolation of cathode lines may be achieved through the use of cathode separators. Typically a number of displays are fabricated on a single substrate and at the end of the fabrication process the substrate is scribed, and the displays separated. An encapsulant such as a glass sheet or a metal can is utilized to inhibit oxidation and moisture ingress.

The edges or faces of the banks are tapered onto the surface of the substrate as shown, typically at an angle of between 10 and 40 degrees. The banks present a hydrophobic surface in order that they are not wetted by the solution of deposited organic material and thus assist in containing the deposited material within a well. This is achieved by treatment of a bank material such as polyimide with an  $O_2/CF_4$  plasma as disclosed in EP 0989778. Alternatively, the plasma treatment step may be avoided by use of a fluorinated material such as a fluorinated polyimide as disclosed in WO 03/083960. Numerous other bank structures are known to the skilled person. For example, the bank may comprise a plurality of layers of the same or different materials, for example a hydrophilic layer capped with a hydrophobic layer. The bank may also comprise an undercut, i.e. the aperture defined by the bank is smaller than the surface area of the base of the well as disclosed in, for example, WO 2005/076386.

The bank and separator structures may be formed from resist material, for example using a positive (or negative) resist for the banks and a negative (or positive) resist for the separators; both these resists may be based upon polyimide and spin coated onto the substrate, or a fluorinated or fluorinated-like photoresist may be employed.

### EXAMPLES

An interlayer formulation for an interlayer material (hole transport material) termed interlayer 1 is a solution of solid material comprising 0.28% solids in Anisole/Phenoxytoluene 1-1). When printed this formulation gave film profiles (15nm) with edge thickening (up to 40nm). Edge thickening is detrimental to device performance as:

- i) the EL ink is printed causing a decrease in device lifetime
- ii) The film profile of the subsequently printed EL layer is dependent on the IL profile. Therefore if the IL film edge thickens then the EL layer will show edge thinning. Variation in the thickness of the EL film across a pixel leads to non-uniform emission and a decrease in device efficiency and lifetime.

This work of the present inventors has demonstrated new solvent combinations for interlayer inks to eliminate interlayer edge thickening.

Table 1 shows the physical properties of the solvents used in the novel compositions in accordance with the present invention. All these formulations were successful in eliminating edge thickening.

| Solvent                                                   | Solvent BP °C     | Solvent ST mN/m  | Solvent Viscosity mPa.s | Motivation                                                  |
|-----------------------------------------------------------|-------------------|------------------|-------------------------|-------------------------------------------------------------|
| Dicyclohexyl 50% /Anisole 50% (A/DC1)                     | 227<br>154        | 32<br>34         | 3.4<br>1                | DC: Less favourable                                         |
| Phenoxytoluene /Dicyclohexyl 49.5% Anisole 50% (P/DC/A80) | 271<br>227<br>154 | 38.7<br>32<br>34 | 5.0<br>3.4<br>1         | P has been added to above formulation to decrease roughness |
| 1- tetralone 80% /Mesitylene 20% (TET/MES9)               | 255<br>165        | 43<br>29         | 8.6<br>0.6              | TET: High viscosity-high surface tension                    |
| Mesitylene 60% /Benzylbenzoate 40% (MES/BZB2)             | 165<br>323        | 29<br>43         | 0.6<br>10               | BZB: High viscosity-high surface tension                    |
| 1-methoxynaphtalene 50% /Mesitylene 50% (MON/MES1)        | 270<br>165        | 43<br>29         | 7.2<br>0.6              | MON: High viscosity-high surface tension                    |

**Table 1**

Figures 4 to 6 show derived interlayer film profiles when printed onto PEDOT (PD239). The A/P1 formulation which is in current use shows edge thickening whereas the new formulations give slight edge thinning.

Figure 4 shows derived interlayer film profiles when printed onto PEDOT (PD239). The A/P1 formulation which is in its current use shows edge thickening whereas the two new formulations (A/DC1 and TET/MES9) give slight edge thinning. The A/DC1 formulation also gave rough films probably caused by the insolubility of the polymer in this particular solvent.

A/P1 = Anisole-3-Phenoxytoluene (1-1)

A/DC1 = Anisole-Dicyclohexyl (1-1)

TET/MES9 = 1-tetralone-Mesitylene (8-2) (NEW FORMULATION 2)

Figure 5 shows the results of different amounts of Phenoxytoluene which was added to the A/DCI to reduce the roughness. It can be seen from the graph below that only 0.5% addition of the Phenoxytoluene (P/DC/A 81: (NEW FORMULATION 1)) decreases the roughness sufficiently and maintains the slightly domed profile.

Figure 6 shows the results of the effect of 1-tetralone (high boiling point solvent which has a high viscosity and high surface tension) being confirmed by two more formulations.

MON/MES1: 1-methoxynaphthalene (50%):Mesitylene (50%) (NEW FORMULATION 3)

MES/BZB2: Mesitylene (60%):Benzylbenzoate (40%) (NEW FORMULATION 4)

## CLAIMS

1. A composition suitable for ink-jet printing, nozzle coating, spray coating, roll printing, dip coating, slot coating, or flexographic printing of an opto-electrical device, which composition comprises a semiconducting hole transport material, hole injection material, light-emitting polymer material, electron transport material, or electron injection layer material, a first solvent and a second solvent, the first solvent having a higher boiling point and a greater viscosity than the second solvent, wherein the solvents are miscible with one another and the viscosity of the first solvent is in the range of 5 to 12 mPas.
2. The composition of claim 1 wherein the viscosity of the first solvent is greater than 6 mPas.
3. A composition according to claim 1 or 2, wherein the viscosity of the first solvent is greater than 7 mPas.
4. The composition of any preceding claim wherein the first solvent is any of 1-tetralone, benzylbenzoate and 1 methoxynaphthalene o-xylene, mixed-xylene, ethylbenzene, propylbenzene, butylbenzene.
5. The composition of any preceding claim wherein the second solvent is any of mesitylene, o-xylene, mixed-xylene, ethylbenzene, propylbenzene, butylbenzene.
6. The composition of any preceding claim wherein the first solvent has a boiling point between 250 and 350°C.
7. The composition of any preceding claim wherein the second solvent has a boiling point between 100 and 200°C.

8. The composition of any preceding claim comprising a semiconducting hole transport material, wherein the semiconducting hole transport material comprises a polymer having a molecular weight in the range of 40,000 to 400,000 Daltons.
9. The composition of any preceding claim comprising a semiconducting hole transport material, wherein the semiconducting hole transport material comprises a polymer having a molecular weight of at least 350,000 Daltons.
10. A composition according to claim 8 or claim 9, wherein the concentration of the semiconducting hole transport material in the composition is 0.8 w/v% or less.
11. The composition of any preceding claim, wherein the ratio of the first solvent to the second solvent is 1:1.
12. The composition of any preceding claim comprising a semiconducting hole transport material, wherein the hole transport material is cross linkable due to the presence of cross linkable groups.
13. The composition of any preceding claim comprising a semiconducting hole transport material, wherein the hole transport material comprises a polymer having a triarylamine repeat unit.
14. The composition of any preceding claim comprising a semiconducting hole transport material, wherein the hole transport material is a copolymer of a triarylamine repeat unit and a second repeat unit.
15. A composition according to claim 14, wherein the second repeat unit is a fluorene repeat unit.
16. A method of forming an organic light-emitting device including the steps of:

- a. providing an anode layer;
- b. optionally providing a conducting hole injecting layer on the anode layer;
- c. depositing a composition as defined in any one of claims 1 to 15 on the anode or hole injecting layer by ink-jet printing to form a semiconducting hole transport layer, provided that when the semiconducting hole transport material is deposited by ink-jet printing then the semiconducting hole transport material is deposited on a hole injecting layer.

17. A method of forming an organic light-emitting device including the step of depositing a composition as defined in any one of claims 1 to 15 by ink-jet printing to form a semiconducting hole transport layer.

18. A method according to claim 16 or claim 17, said method including a further step of baking the semiconducting hole transport layer by heating.

19. A method according to any claim 17 or 18, wherein deposition of the said composition is onto an anode or a conducting hole injecting layer.

20. A method according to any one of claims 16 to 21, further including the steps of: depositing a luminescent layer on the semiconducting hole transport layer, optionally depositing an electron transport layer on the luminescent layer, and depositing a cathode on the luminescent layer or electron transport layer, where present.

21. A method according to any one of claims 16 to 20, further including a step of removing solvent from the semiconducting hole transport layer.

22. An organic light-emitting device made by a method according to any one of claims 16 to 21.

23. A full colour display comprising an organic light-emitting device according to claim 22.

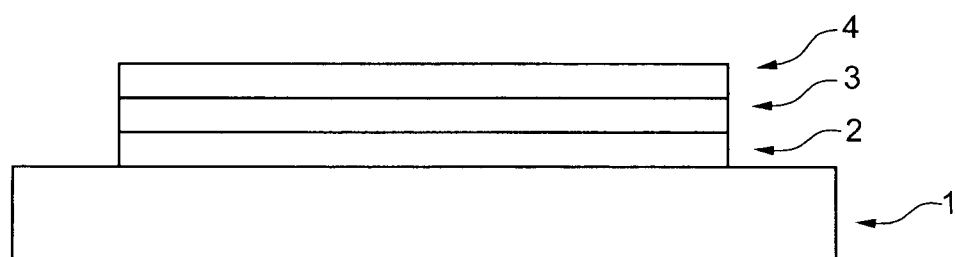


Fig. 1

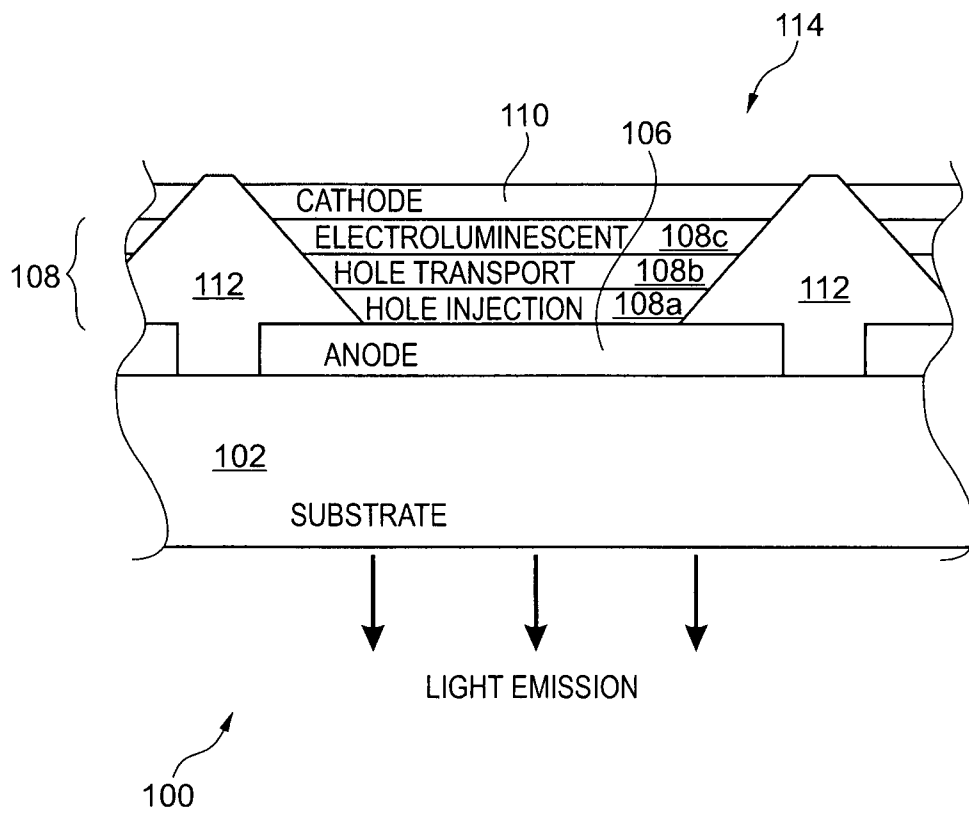


Fig. 2

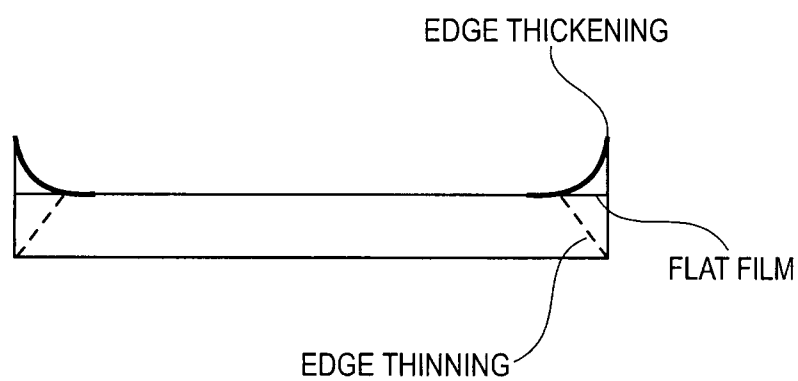


Fig. 3

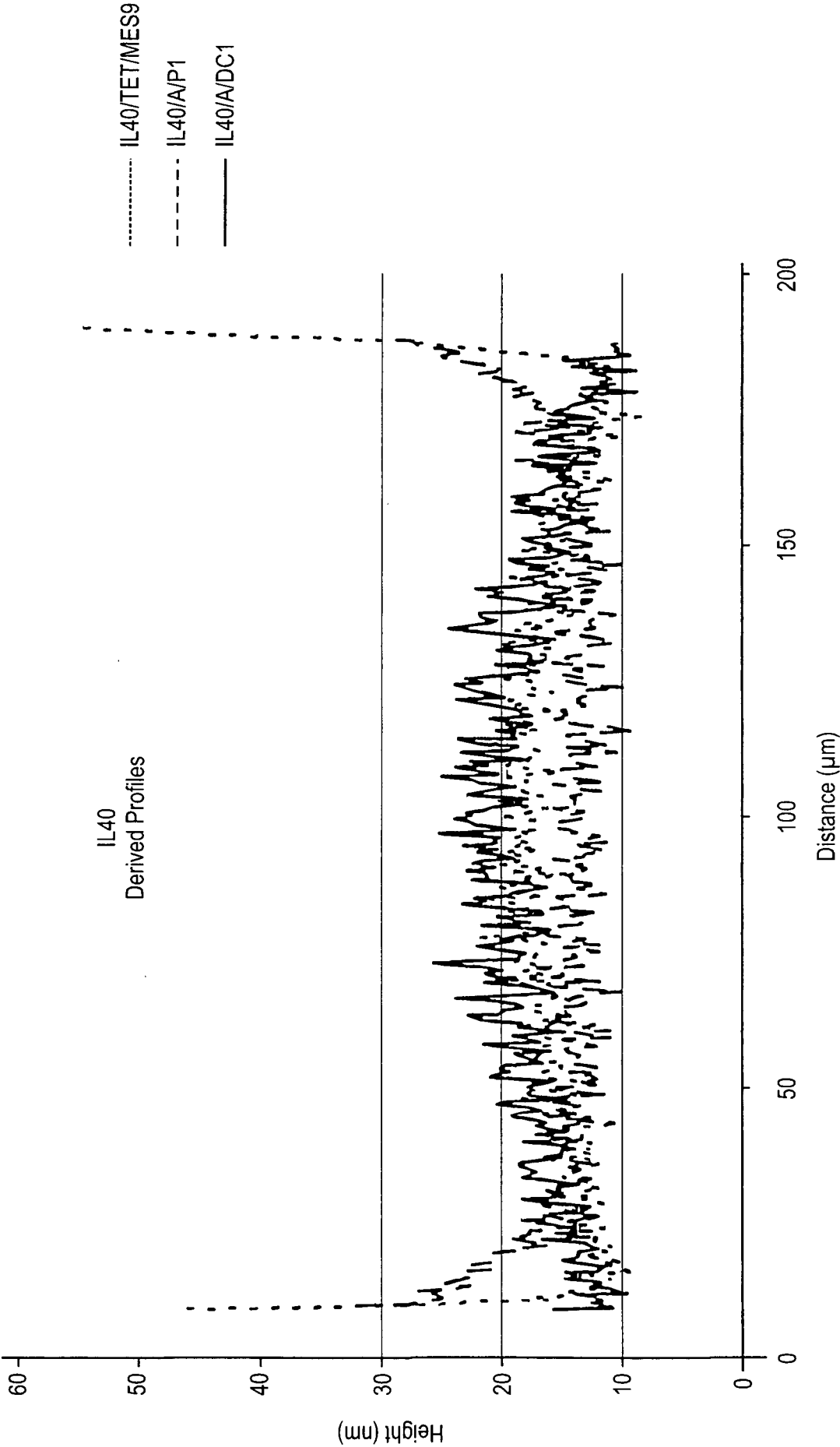


Fig. 4

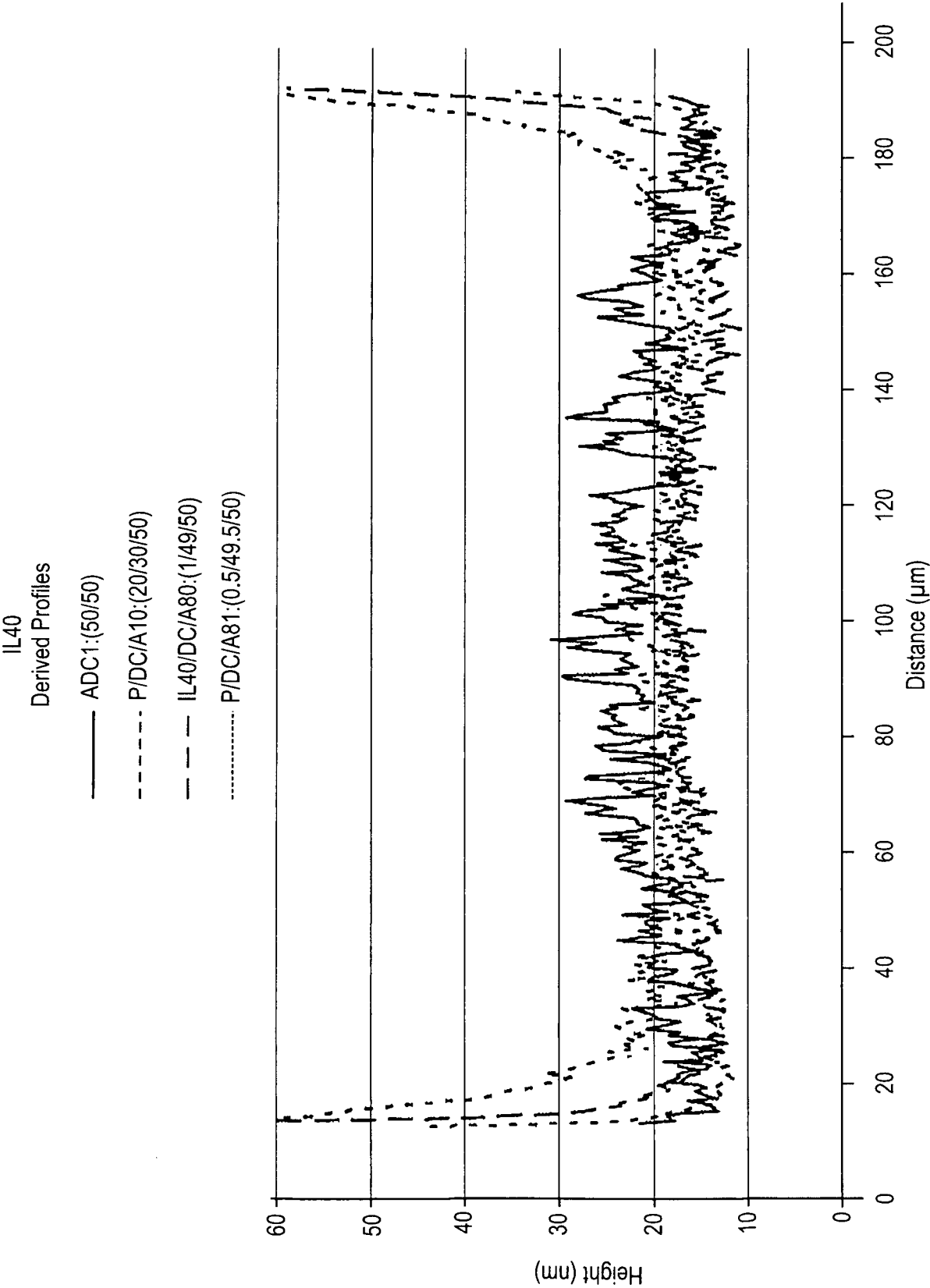


Fig. 5

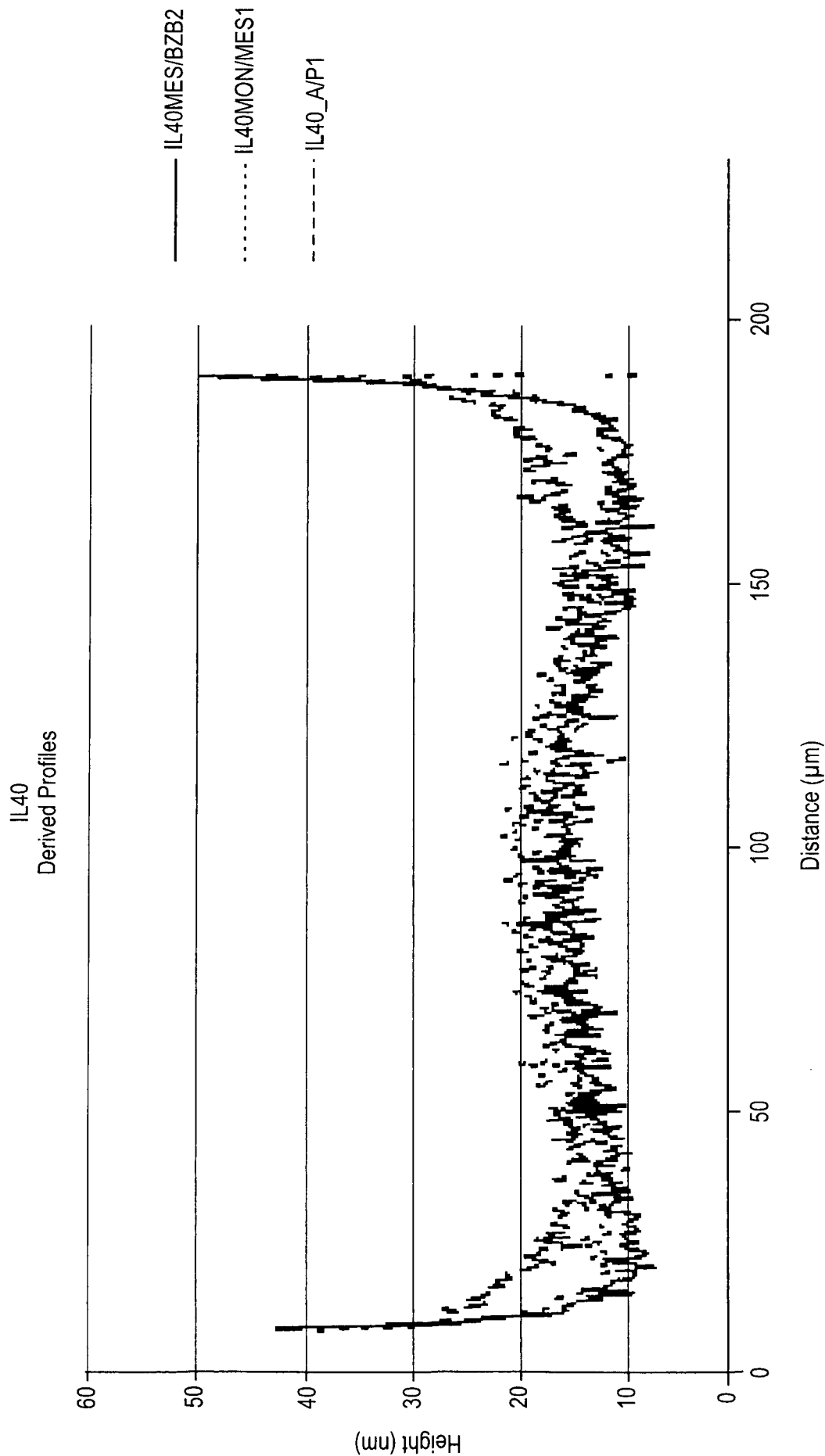


Fig. 6

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2010/000019

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. H01L51/54 B41J2/21

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)  
H01L B41J

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

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

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                           | Relevant to claim No.                 |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|
| X         | EP 1 894 976 A1 (SUMITOMO CHEMICAL CO [JP]) 5 March 2008 (2008-03-05)<br><br>figures 1-3; example 7<br>paragraph [0165] - paragraph [0166]<br>paragraphs [0032], [0071], [0072],<br>[0216], [0217], [0218]<br>claims 14,17                   | 1-3,5-8,<br>13-14,<br>16-17,<br>20-22 |
| X         | WO 02/069119 A1 (CAMBRIDGE DISPLAY TECH [GB]; LYON PETER JOHN [GB]; CARTER JULIAN CHARL) 6 September 2002 (2002-09-06)<br><br>page 1, line 9 - line 26<br>page 3, line 9 - line 10<br>page 3, line 20 - line 24<br>figures 1,2,6E; example 1 | 1-4,<br>6-10,<br>13-17,<br>19,21-22   |
| -/--      |                                                                                                                                                                                                                                              |                                       |

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

17 March 2010

Date of mailing of the international search report

26/03/2010

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

Authorized officer

Pusch, Catharina

## INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2010/000019

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                 | Relevant to claim No.     |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------|
| X         | EP 1 083 775 A1 (SEIKO EPSON CORP [JP]<br>SEIKO EPSON CORP [JP]; CAMBRIDGE DISPLAY<br>TECH [G] 14 March 2001 (2001-03-14)<br>paragraphs [0040], [0043], [0054],<br>[0056], [0060]<br>paragraphs [0079] - [0084]<br>-----                           | 1,6-7,<br>11-19,<br>21-22 |
| A         | US 2005/067949 A1 (NATARAJAN SRIRAM [US]<br>ET AL) 31 March 2005 (2005-03-31)<br>paragraphs [0038], [0041]; figures 4,5<br>-----                                                                                                                   | 1,16                      |
| A         | DE 10 2004 007777 A1 (COVION ORGANIC<br>SEMICONDUCTORS [DE])<br>8 September 2005 (2005-09-08)<br>the whole document<br>-----                                                                                                                       | 1,16                      |
| A         | "Dodecylbenzene"<br>INTERNET CITATION<br>1 June 1999 (1999-06-01), XP009131056<br>Retrieved from the Internet:<br>URL: <a href="http://cameochemicals.noaa.gov/chris/DB.pdf">http://cameochemicals.noaa.gov/chris/DB.pdf</a><br>table 9.3<br>----- | 1,16                      |

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB2010/000019

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1(all partially)  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1(all partially)

Claim 1 is contradicted by claim 4 in which as the first solvents o-xylene, mixed xylenes, ethylbenzene, propylbenzene, and butylbenzene are defined. However, none of these solvents falls under the definition of a first solvent of claim 1 having a viscosity in the range of 5 to 12 mPa.s. Moreover, according to page 19, line 5 a composition of anisole (Bp 154 °C, viscosity 1 mPa.s) and phenoxytoluene (Bp 271 °C, viscosity 5 mPa.s) which fulfils the requirements of claim 1 does not solve the problem of levelling out edge thickening. This example thus casts doubt on the intended limitation of the claims. As it is not defined at which temperature the viscosity is to be measured, claim 1 encompasses an indefinite number of compounds having a viscosity in the range of 5 to 12 mPa.s and, hence, an as indefinite number of compositions. For the above three reasons, the definition of claim 1 has been limited to the three solvents used in the application and falling under the definition of claim 1. Claim 1 has been searched as if it was limited to 1-tetralone, benzylbenzoate or 1-methoxynaphthalene as the first solvent.

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

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/000019

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s)                                                                                   | Publication<br>date                                                              |
|-------------------------------------------|----|---------------------|--------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| EP 1894976                                | A1 | 05-03-2008          | WO 2006123741 A1<br>KR 20080007617 A<br>US 2009103284 A1                                                     | 23-11-2006<br>22-01-2008<br>23-04-2009                                           |
| WO 02069119                               | A1 | 06-09-2002          | AU 2002236023 A8<br>EP 1364420 A2<br>JP 4347569 B2<br>JP 2004532096 T                                        | 12-09-2002<br>26-11-2003<br>21-10-2009<br>21-10-2004                             |
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| US 2005067949                             | A1 | 31-03-2005          | WO 2005041322 A1<br>TW 250821 B                                                                              | 06-05-2005<br>01-03-2006                                                         |
| DE 102004007777                           | A1 | 08-09-2005          | CN 1922744 A<br>EP 1716604 A1<br>WO 2005083814 A1<br>JP 2007527624 T<br>KR 20070001138 A<br>US 2007173578 A1 | 28-02-2007<br>02-11-2006<br>09-09-2005<br>27-09-2007<br>03-01-2007<br>26-07-2007 |