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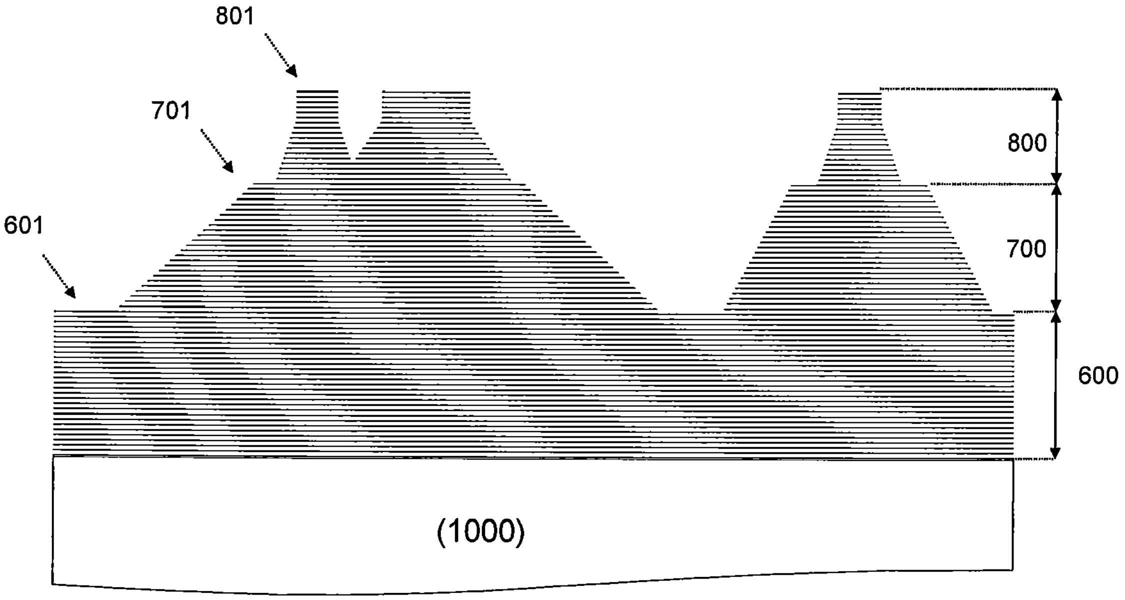
(54) Method of preparing a flexographic printing master

(57) A method for preparing a flexographic printing master wherein an optional floor (600), an optional mesa relief (700) and an image relief (800) are applied in this order on a flexographic printing support (1000) by depositing a plurality of layers of a curable fluid on top of each other characterized in that at least one layer of a curable fluid is deposited by aerosol jet printing

Figure 4



EP 2 574 458 A1

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method for making a flexographic printing master comprising an aerosol jet printing step.

BACKGROUND OF THE INVENTION

[0002] Flexography is a form of printing process which utilizes a flexible relief plate, the flexographic printing master. It is basically an updated version of letterpress that can be used for printing on almost any type of substrate including plastic, metallic films, cellophane, and paper. Flexography is widely used for printing on packaging material, for example food packaging. Also, with flexography continuous patterns, such as for gift wrap and wall paper, can be printed.

[0003] Today flexographic printing masters are prepared by both analogue and digital imaging techniques. Analogue imaging typically uses a film mask through which a flexographic printing precursor is exposed. Digital imaging techniques include:

- Direct laser engraving as disclosed in e.g. EP-As 1710093 and 1936438;
- UV exposure through a LAMS mask wherein LAMS stands for Laser Ablative Mask System as disclosed in e.g. EP-A 1170121;
- Direct UV or violet exposure by laser or LED as disclosed in e.g. US6806018; and
- Inkjet printing as disclosed in e.g. EP-As 1428666 and 1637322.

[0004] The major advantage of an inkjet method for preparing a flexographic printing master is an improved sustainability due to the absence of any processing step and the consumption of no more material as necessary to form a suitable relief image (i.e. removal of material in the non printing areas is no longer required).

[0005] EP-A 641648 discloses a method of making a photopolymer relief-type printing plate wherein a positive or negative image is formed on a substrate by inkjet printing with a photopolymeric ink and subjecting the resulting printed substrate to UV radiation, thereby curing the ink composition forming the image.

[0006] US6520084 discloses a method of preparing flexographic printing masters by inkjet wherein a removable filler material is used to support the relief image being printed and wherein the relief image is grown in inverted orientation on a substrate. Disadvantages of this method are the removal of the filler material and the release of the relief image from the substrate.

[0007] EP-A 1428666 discloses a method of making a flexographic printing master by means of jetting subsequent layers of a curable fluid on a flexographic support. Before jetting the following layer, the previous layer is immobilized by a curing step.

[0008] In US7036430 a flexographic printing master is prepared by inkjet wherein each layer of ink is first jetted and partially cured on a blanket whereupon each such layer is then transferred to a substrate having an elastomeric floor, thereby building up the relief image layer by layer. A similar method is disclosed in EP-A 1449648 wherein a lithographic printing plate is used to transfer such layers of ink to a substrate.

[0009] US2008/0053326 discloses a method of making a flexographic printing master by inkjet wherein successive layers of a polymer are applied to a specific optimized substrate. In US2009/0197013, also disclosing an inkjet method of making a flexographic printing master, curing means are provided to additionally cure, for example, the side surfaces of the image relief being formed. In EP-A 2223803 a UV curable hot melt ink is used. Each of the deposited layers of ink is gelled before a subsequent layer is deposited. After a printing master with sufficient thickness is formed, a curing step is carried out.

[0010] EP-As 1637926 and 1637322 disclose a specific curable jettable fluid for making flexographic printing masters comprising a photo-initiator, a monofunctional monomer, a polyfunctional monomer or oligomer and at least 5 wt. of a plasticizer. The presence of the plasticizer is necessary to obtain a flexographic printing master having the necessary flexibility. Also in EP-A 2033778, the curable jettable fluid for making a relief image by inkjet on a sleeve body contains a plasticizer.

[0011] A flexographic printing master formed on a support by an inkjet method typically comprises an elastomeric floor, an optional mesa relief and an image relief as disclosed in EP-A 2199082.

[0012] To realize a high resolution flexographic printing master with such inkjet methods it is advantageous to use a print head with small nozzle diameters, for example producing 3 pl fluid droplets. Print heads with such small nozzle diameters however require low viscosity fluids. The requirement for such a low viscosity however imposes constraints on the choice of the ingredients of the fluid. For example it limits the amount of monomers having a high viscosity or the amount of plasticizers, while often a high amount of such ingredients is preferred to prepare flexographic printing masters with optimal physical properties.

[0013] It would therefore be advantageous to realize a method for preparing high resolution flexographic printing masters having optimal physical properties, the method having the same advantages as the inkjet method described in the prior art and using fluids of which the viscosity does not have to be very low.

SUMMARY OF THE INVENTION

[0014] It is an object of the present invention to provide a method for preparing a flexographic printing master having a high resolution and good physical properties.

[0015] The object of the present invention is realised with by the method for preparing a flexographic printing master as defined in claim 1.

[0016] Preferred embodiments are defined in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

Figure 1 gives a schematic presentation of an aerosol jet printing system.

Figure 2 illustrates a difference between inkjet printing and aerosol jet printing.

Figure 3 gives a schematic presentation of a preferred embodiment of an apparatus to carry out the method of the present invention.

Figure 4 gives a schematic presentation of a preferred embodiment a flexographic printing master.

DETAILED DESCRIPTION OF THE INVENTION

Aerosol Jet Printing

[0018] The present invention relates to a method for preparing a flexographic printing master comprising an aerosol jet printing step.

[0019] Aerosol Jet Printing, which has been developed by Optomec, preserves most of the advantages of inkjet printing, while reducing many of its limitations. The technique is developed for use in the field of printed electronics. The technique is disclosed in for example US2003/0048314, US2003/0020768, US2003/0228124 and WO2009/049072. An Aerosol Jet Print Engine is commercially available from Optomec, for example the Aerosol Jet Printer OPTOMEC AJ 300 CE. More details on the Aerosol Jet Printing technique and engine are found on the Optomec website www.optomec.com.

[0020] Virtually any liquid having a viscosity less than 5000 mPa.s can be deposited using the Aerosol Jet Printing technique while inkjet printing requires fluids having a viscosity of less than 20 mPa.s.

[0021] As already mentioned above, using higher viscous fluids may be advantageous when preparing flexographic printing masters having optimal physical properties.

[0022] In Aerosol Jet Printing a collimated beam of material is dispensed on a substrate. This allows the resolution to be maintained over a wide range of standoff (head to substrate) distances. This enables larger standoff distances to be used than are possible with inkjet printing. The differences between inkjet and Aerosol Jet Printing are schematically shown in Figure 2. In inkjet, the drops are typically of low density. The standoff (500) between the nozzle and the substrate is usually about 1 mm. The droplets spread out upon leaving the nozzle, and the system is normally optimized to achieve optimum results at the fixed standoff distance. In Aerosol Jet Printing, a collimated beam of material is formed which is then deposited on the substrate. Therefore, standoff distances from 1 to 5 mm can be used without loss of resolution. This feature is very important for printing features over an existing topology as found in many electrical devices and circuits, and enables conformal printing, which is the application for which the Aerosol Jet Printing technology was originally developed. The thickness of the total relief image (floor - mesa relief and image relief) of a flexographic printing master may be up to several mm. When using inkjet printing and when the print head does not move in the z direction, the standoff distance between the print head and the lower layers of the printing master may be several mm resulting in a different resolution of the lower an upper layers making up the printing master. However, by using such a collimated beam of material, the resolution of the lower and the upper layers will almost not vary when using Aerosol Jet Printing.

[0023] In an Aerosol Jet Printing system, rather than producing individual droplets of ink, an aerosol is produced, focused and directed toward the substrate. A schematic presentation of such an Aerosol Jet

[0024] Printing system is given in Figure 1. The basic system consists of two key components: a first module (200) for forming an aerosol (210) from a fluid (220) and a second module (300) focussing the aerosol (210) and depositing the aerosol droplets on a substrate (400). Similar to continuous inkjet, this aerosol stream can be shuttered to interrupt the stream.

[0025] As described above, one of the key advantages of the Aerosol Jet Printing system is its large materials window. Aerosols can be formed from fluids as viscous as 5000 mPa.s. In Aerosol Jet Printing printing, two different ways of forming an aerosol can be employed, depending on the characteristics of the material to be deposited. An ultrasonic transducer can be used for nebulizing low viscosity fluids (0.7 to 10 mPa.s). Here, a piezoelectric transducer produces high frequency pressure waves, which are transmitted through a coupling fluid (typically water) into the deposition fluid. This atomization technique works best for suspended particles of less than 50 nm. For higher viscosity fluids (10 to 5000 mPa.s) or larger suspended particles (< 0.5 μm) pneumatic atomization is used. In this technique, a high velocity gas stream is used to shear the liquid stream into droplets.

[0026] In both of these atomization techniques, a dense aerosol jet is produced. One of the most unique features of the Aerosol Jet Printing System is that the aerosol stream can be focused to a fine, collimated (the cross sectional diameter does not vary as a function of the distance from the nozzle) beam. Here, the focusing gas (300) surrounds the aerosol completely so that droplets do not touch the inner walls of the nozzle, eliminating clogging and other problems. This aerosol jet focusing gives rise to a jet diameter which is much smaller than that of the nozzle orifice. A variety of line widths can be produced, from about 10 to 150 μm.

Method of preparing a flexographic printing master

[0027] Several methods of preparing a flexographic printing master by inkjet are disclosed in EP-As 1637322, 2199081, 2199082 and WO2008/077850 and in the unpublished EP-A 10163064.8 (filed 2010-05-18). In all those methods, subsequent layers of a curable fluid are jetted by an inkjet print head and subsequently at least partially cured.

[0028] A preferred flexographic printing master according to the present invention is disclosed in EP-A 2199082. It typically comprises on a substrate (1000), preferably a sleeve body, in this order, a floor (600), a mesa relief (700) and an image relief (800). EP-A 2199082 disclosed a method for preparing such a flexographic printing master with inkjet.

[0029] In one embodiment of the present invention, the above mentioned methods of preparing a flexographic printing master are modified in that all layers are now deposited by the aerosol jet printing technique instead of the inkjet printing technique.

[0030] However, it may be advantageous to combine both the inkjet printing and aerosol printing technique. For example, to form the floor and the mesa relief, where resolution is not an issue, inkjet printing may be used to optimize the throughput of the method, for example by using large fluid droplets. The image relief, where resolution must be as high as possible, may then be deposited using the aerosol jet printing technique.

[0031] In another embodiment, only the upper most layer (the top layer of the image relief) is deposited using aerosol jet printing, while all other layers are deposited using inkjet printing. High viscous fluids may then be used to deposit the top layer to optimize the properties of the printing areas of the flexographic printing master. To further optimize the flexographic printing master, more then one top layer, for example two, three or more, may be applied using aerosol jet printing.

[0032] In still another embodiment, the upper most layer(s) of the floor and the mesa relief may be applied using aerosol jet printing while the other layers are applied using inkjet.

[0033] To further optimize the throughput of the method, the floor may be precoated on a sleeve body by conventional coating techniques. The mesa relief and the image relief are then applied on the precoated floor by aersol jet printing, or the combination aerosol jet printing - inkjet printing. Also, the image relief may be directly applied on the floor.

Curable fluid

[0034] As described above, the method according to the present invention may use aerosol jet printing only, or a combination of aerosol jet printing and inkjet printing.

[0035] The same fluid may be used in both the aerosol jet printing step and the inkjet printing step but preferably different fluids are used, optimized towards the printing technique, hereinafter referred to as the curable aerosol jet fluid and the curable inkjet fluid. For example, for the aerosol jet printing step high viscous fluids are preferably used to optimize the properties of the obtained flexographic printing master.

[0036] Typical ingredients for both types of fluids are preferably selected from the group consisting of a monofunctional (meth)acrylate monomer, a difunctional (meth)acrylate monomer, a multifunctional (meth)acrylate monomer or oligomer, a low viscous monofunctional urethane acrylate oligomer (especially for curable inkjet fluid), a higher viscous mono-or multifunctional urethane acrylate (especially for the curable aerosol jet fluid), an initiator, a plasticizer, an inhibitor, an elastomeric binder, a surfactant, a colorant, a solvent, an humectants, a biocide.

Monofunctional (meth)acrylate monomer

[0037] The curable fluid may comprises a monofunctional (meth)acrylate monomer. Any monofunctional (meth)acrylate monomer, such as disclosed for example in EP-A 1637322, paragraph [0055], may be used.

[0038] However, the curable fluid preferably comprises a cyclic monofuntional (meth)acrylate monomer. Examples of such cyclic monofunctional (meth)acrylates are isobornyl acrylate (SR506D from Sartomer), tetrahydrofurfuryl methacrylate (SR203 from Sartomer), 4-t.butylcyclohexyl arylate (Laromer TBCH from BASF), dicyclopentadienyl acrylate (Laromer DCPA from BASF), dioxalane functional acrylates (CHDOL10 and MEDOL10 from San Esters Corporation), cyclic trimethylolpropane formal acrylate (SR531 from Sartomer), 2-phenoxyethyl acrylate (SR339C from Sartomer), 2-phenoxyethyl methacrylate (SR340 from Sartomer), tetrahydrofurfuryl acrylate (SR285 from Sartomer), 3,3,5-trimethyl cyclohexyl acrylate (CD420 from Sartomer).

[0039] Particularly preferred cyclic monofunctional (meth)acrylates monomers are isobornyl acrylate (IBOA) and 4-t.butylcyclohexyl arylate (Laromer TBCH from BASF).

[0040] The amount of the cyclic monofunctional (meth)acrylate monomer is preferably at least 25 wt.%, more preferably at least 30 wt.%, relative to the total weight of the curable fluid.

Difunctional (meth)acrylate monomer

[0041] A preferred difunctional (meth)acrylate monomer is a polyalkylene glycol di(meth)acrylate. Such compounds have two acrylate or methacrylate groups attached by an ester linkage at the opposite ends of a hydrophilic polyalkylene glycol. Typically, the longer the length of the polyalkylene chain, the softer and more flexible the obtained layer after curing.

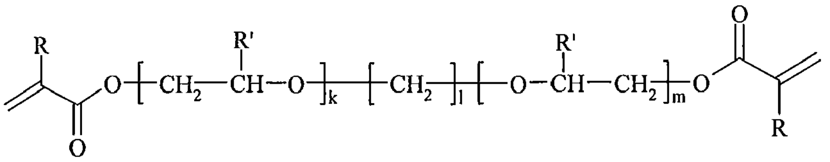
[0042] Examples of such polyalkylene glycol di(meth)acrylates include: 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, dipropylene glycol diacrylate, ethylene glycol dimethacrylate, polyethylene glycol (200) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (400) dimethacrylate, polyethylene glycol (600) diacrylate, polyethylene glycol (600) dimethacrylate, polyethylene glycol dimethacrylate, polypropylene glycol (400) dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tripropylene glycol diacrylate, and combinations thereof. The number between brackets in the above list refers to the Molecular Weight (MW) of the polyalkylene chain.

[0043] Highly preferred polyalkylene glycol diacrylates are polyethylene glycol diacrylates. Specific examples of commercially available polyethylene glycol diacrylate monomers include SR259 [polyethylene glycol (200) diacrylate], SR344 [polyethylene glycol (400) diacrylate], SR603 [polyethylene glycol (400) dimethacrylate], SR610 [polyethylene glycol (600) diacrylate], SR252 [polyethylene glycol (600) dimethacrylate], all Sartomer products; EBECRYL 11 [poly ethylene glycol diacrylate from Cytec; Genomer 1251 [polyethylene glycol 400 diacrylate] from Rahn. Polyethylene glycol (600) diacrylate, available as SR610 from Sartomer, is particularly preferred.

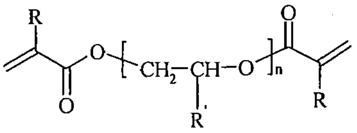
[0044] Other preferred difunctional acrylate or methacrylate monomers are e.g. butane diol diacrylate, alkoxylated hexanediol diacrylate, alkoxylated neopentyl glycol diacrylate and alkoxylated hexanediol dimethacrylate.

[0045] The amount of the difunctional (meth)acrylate monomer is preferably at least 10 wt.% of the total monomer content.

[0046] Particularly preferred difunctional (meth)acrylate monomers are those according to Formula I or II,



Formula I



Formula II

wherein
k and m in Formula I is an integer ranging from O to 5,
1 in Formula I is an integer ranging from 1 to 20

n in Formula II is 1, 2, 3 or 4,
R is H or CH_3, and
R' is H or an alkyl group.

[0047] Difunctional (meth)acrylate monomers according to Formula I are typically derived from diols containing an -(CH_2)- backbone. Preferred compounds according to Formula I are polyoxytetramethylene diacrylate (Blemmer ADT250); 1,9 nonanediol diacrylate; 1,6 hexanediol diacrylate (SR238); 1,6 hexanediol dimethacrylate (SR239); 1,4 butanediol diacrylate (SR213); 1,2 ethanediol dimethacrylate (SR206); 1,4 butanediol dimethacrylate (SR214); ethoxylated 1,6 hexanediol diacrylate (Miramer M202)

[0048] Difunctional (meth)acrylate monomers according to Formula II are typically derived from diols containing a glycol ether backbone. The R' group in Formula II is preferably H or methyl. Preferred compounds according to Formula II are dipropyleneglycol diacrylate (DPGDA, SR508), diethylene glycol diacrylate (SR230), triethyleneglycol diacrylate (SR272), 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, dipropylene glycol diacrylate, ethylene glycol dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tripropylene glycol diacrylate, and combinations thereof.

[0049] The amount of the difunctional acrylate monomer according to Formula I or II is at least 1 wt.%, preferably at least 5 wt.%, more preferably at least 7.5 wt.%, relative to the total weight of the curable fluid.

<u>Multi functional (meth)acrylate monomer</u>

[0050] The curable fluid further comprises a tri-, tetra- or penta-functional (meth)acrylate monomer. It has been observed that the hardness of the cured layer obtained from the curable fluid becomes too high when too much tri-, tetra- or penta-functional (meth)acrylate monomer is present in the fluid. The Shore A hardness of the cured layer must be kept below 80, to ensure good physical properties of the flexographic printing master. It has been observed that the maximum concentration of the tri-, tetra- or penta-functional (meth)acrylate monomer to ensure a proper hardness depends on their functionality. Typically, the higher their functionality, the lower their maximum allowable concentration to ensure a Shore A hardness below 80. In addition to its effect on the hardness, the functionality of the tri-, tetra- or penta-functional (meth)acrylate monomers also influences their viscosity, and thus also the viscosity of the curable fluid. Typically, the higher their functionality, the higher their viscosity. As the viscosity of the curable inkjet fluid, measured at jetting temperature, is preferably below 15 mPa.s, this also limits the maximum concentration of the tri- tetra- or penta-functional (meth)acrylate monomer in the jettable fluid.

[0051] Preferably, the maximum concentration of the tri-, tetra- or penta-functional (meth)acrylate monomer, dependent on their viscosity, is as depicted in the following table.

visco (mPa.s) functionality	< 100	100 - 250	250 - 5000	> 5000
3	20 wt.%	17.5 wt.%	15 wt.%	10 wt.%
4	15 wt.%	12.5 wt.%	10 wt.%	7.5 wt.%
5	10 wt.%	8 wt.%	6 wt.%	4 wt.%

[0052] The minimum concentration is preferably 0.5 wt.%, more preferably 1 wt.%).

[0053] For the curable aerosol jet fluid, the higher viscosities are allowable as described above. Therefore, higher concentrations of multifunctional (meth)acrylate monomers may be used.

[0054] Preferred examples are ditrimethylol propane tetraacrylate (DTMPTA), glycerol triacrylate and their alkoxylated, i.e. ethoxylated or propoxylated, derivatives.

[0055] Specific compounds are trimethylol propane tetraacrylate (TMPTA), commercially available as Miramer M300; propoxylated TMPTA, commercially available as SR492; ethoxylated TMPTA, commercially available as Miramer M3130; DTMPTA, commercially available as SR355; propoxylated glyceryl triacrylate, commercially available as SR9021 and SR9020.

[0056] Other specific compounds are dipentaerythritol pentaacrylate (DIPEPA), commercially available as SR399LV; tri-acrylate esters of pentaerythritol, such as pentaerythritol triacrylate (PETIA); tetraacrylate esters of pentaerythritol, such as PETRA, commercially available as SR295; ethoxylated PETRA, commercially available as SR494; alkoxylated PETRA, commercially available as Ebecryl 40.

Urethane acrylate oligomer

[0057] The curable fluid, especially the curable inkjet fluid, may further contain monofunctional urethane acrylate oligomers.

[0058] Urethane acrylates oligomers are well known and are prepared by reacting polyisocyanates with hydroxyl alkyl acrylates, usually in the presence of a polyol compound. Their functionality (i.e. number of acrylate groups) varies from 1 to 6. A lower functionality results in lower reactivity, better flexibility and a lower viscosity. The polyol compound forms the backbone of the urethane acrylate. Typically the polyol compounds are polyether or polyester compounds with a functionality (hydroxyl groups) ranging from two to four. Polyether urethane acrylates are generally more flexible, provide lower cost, and have a slightly lower viscosity and are therefore preferred.

[0059] Commercially available urethane (meth)acrylates are e.g. CN9170, CN910A70, CN966H90, CN962, CN965, CN9290 and CN981 from SARTOMER; BR-3741B, BR-403, BR-7432, BR-7432G, BR-3042, BR-3071 from BOMAR SPECIALTIES CO.; NK Oligo U-15HA from SHIN-NAKAMURA CHEMICAL CO. Ltd.; Actilane 200, Actilane SP061, Actilane 276, Actilane SP063 from AKZO-NOBEL; Ebecryl 8462, Ebecryl 270, Ebecryl 8200, Ebecryl 285, Ebecryl 4858, Ebecryl 210, Ebecryl 220, Ebecryl 1039, Ebecryl 1259 and IRR160 from CYTEC; Genomer 1122 and Genomer 4215 from RAHN A.G. and VERBATIM HR50 an urethane acrylate containing liquid photopolymer from CHEMENCE.

[0060] The curable inkjet fluid preferably comprises monofunctional urethane acrylate oligomers, more preferably monofunctional aliphatic urethane acrylates, having a very low viscosity of 100 mPa.s or lower at 25°C, like for example Genomer 1122 (2-acrylic acid 2-{[(butylamino) carbonyl]oxy}ethyl ester, available from Rahn AG) and Ebecryl 1039 (available from Cytec Industries Inc.).

[0061] The total amount of the monofunctional urethane acrylate oligomer is preferably at least 5 wt.%, more preferably at least 7.5 wt.%, relative to the total weight of the curable fluid.

[0062] Because viscosity of the aerosol jet fluids is not that restricted as for the inkjet fluids, the aerosol jet fluid may contain both mono- and multifunctional urethane acrylates

Other monomers or oligomers

[0063] Additional mono- or multifunctional monomers or oligomers may be used to further optimize the properties of the curable fluid.

Initiators

[0064] The curable fluid comprises an initiator which, upon exposure to radiation or heat, initiates the curing, i.e. polymerization, of the jetted droplets.

[0065] However, it is also possible to carry out the curing by electron beam radiation where the presence of an initiator is not mandatory.

[0066] Preferably a photo-initiator is used which upon absorption of actinic radiation, preferably UV-radiation, forms high-energy species (for example radicals) inducing polymerization and crosslinking of the monomers and oligomers of the jetted droplets.

[0067] A combination of two or more photo-initiators may be used. A photo-initiator system, comprising a photo-initiator and a co-initiator, may also be used. A suitable photo-initiator system comprises a photo-initiator, which upon absorption of actinic radiation forms free radicals by hydrogen abstraction or electron extraction from a second compound, the co-initiator. The co-initiator becomes the actual initiating free radical.

[0068] Irradiation with actinic radiation may be realized in two steps, each step using actinic radiation having a different wavelength and/or intensity. In such cases it is preferred to use 2 types of photo-initiators, chosen in function of the different actinic radiation used.

[0069] Suitable photo-initiators are disclosed in EP-A 1637926 paragraph [0077] to [0079].

[0070] To avoid extraction of the photo-initiator out of the flexographic printing master during printing, copolymerizable photo-initiators (and/or co-initiators) such as disclosed in the unpublished EP-A 10195896.5 (filed on 2010-12-20) may be used.

[0071] A preferred total amount of initiator is 1 to 10 wt.%, more preferably 2.5 to 7.5 wt.%, of the total curable fluid weight.

Plasticizer

[0072] A plasticizer, as disclosed in for example EP-A 1637926 ([0085] - [0091]) may be added to the curable fluid. Such a plasticizer is typically a substance which, when added to a flexographic printing master, increases the softness and flexibility of that printing master. However, as mentioned above, such plasticizers may migrate to the surface of the relief image or may be extracted out of the relief image by the flexo printing ink during printing. For that reason, it is preferred to use a copolymerizable plasticizing monomer such as a low Tg monomer of which the corresponding homopolymer has a glass transition temperature below -15°C or diallylphthalate, as disclosed in the unpublished EP-A 10195895.7 (filed on 2010-12-20).

Inhibitors

[0073] Suitable polymerization inhibitors include phenol type antioxidants, hindered amine light stabilizers, phosphor type antioxidants, hydroquinone monomethyl ether commonly used in (meth)acrylate monomers, and hydroquinone, methylhydroquinone, t-butylcatechol, pyrogallol may also be used. Of these, a phenol compound having a double bond in molecules derived from acrylic acid is particularly preferred due to its having a polymerization-restraining effect even when heated in a closed, oxygen-free environment. Suitable inhibitors are, for example, Sumilizer® GA-80, Sumilizer GM and Sumilizer® GS produced by Sumitomo Chemical Co., Ltd. Since excessive addition of these polymerization inhibitors will lower the sensitivity to curing of the curable jettable liquid, it is preferred that the amount capable of preventing polymerization be determined prior to blending. The amount of a polymerization inhibitor is generally between 200 and 20 000 ppm of the total curable fluid weight.

Oxygen inhibition

[0074] Suitable combinations of compounds which decrease oxygen polymerization inhibition with radical polymerization inhibitors are: 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1 and 1-hydroxy-cyclohexyl-phenyl-ketone; 1-hydroxy-cyclohexyl-phenyl-ketone and benzophenone; 2-methyl-1[4-(methylthio)phenyl]-2-morpholinopropane-1-on and diethylthioxanthone or isopropylthioxanthone; and benzophenone and acrylate derivatives having a tertiary amino group, and addition of tertiary amines. An amine compound is commonly employed to decrease an oxygen polymerization inhibition or to increase sensitivity. However, when an amine compound is used in combination with a high acid value compound, the storage stability at high temperature tends to be decreased. Therefore, specifically, the use of an amine compound with a high acid value compound in inkjet printing should be avoided.

Synergist additives may be used to improve the curing quality and to diminish the influence of the oxygen inhibition. Such additives include, but are not limited to ACTILANE® 800 and ACTILANE® 725 available from AKZO NOBEL, Ebecryl® P115 and Ebecryl® 350 available from UCB CHEMICALS and CD 1012, Craynor CN 386 (amine modified acrylate) and Craynor CN 501 (amine modified ethoxylated trimethylolpropane triacrylate) available from CRAY VALLEY.

[0075] The content of the synergist additive is in the range of 0 to 20 wt.%, preferably in the range of 5 to 15 wt.%, based on the total weight of the curable fluid.

Elastomeric binder

[0076] The elastomeric binder may be a single binder or a mixture of various binders. The elastomeric binder is an elastomeric copolymer of a conjugated diene-type monomer and a polyene monomer having at least two non-conjugated double bonds, or an elastomeric copolymer of a conjugated diene-type monomer, a polyene monomer having at least two non-conjugated double bonds and a vinyl monomer copolymerizable with these monomers. Preferred elastomeric binders are disclosed in EP-A 1637926 paragraph [0092] and [0093].

[0077] Due to their high molecular weight, the addition of elastomeric binders may cause an increase in viscosity of the curable fluid. Therefore, the amount of elastomeric binder is preferably less than 5 wt.% for the curable inkjet fluid. In a particular preferred embodiment, no elastomeric binder is added to the curable inkjet fluid. As viscosity is not an issue, more elastomeric binder, preferably more than 5 wt.%, more preferably more than 10 wt.%, may be used for the curable aerosol jet fluid.

Surfactants

[0078] The surfactant(s) may be anionic, cationic, non-ionic, or zwitterionic and are usually added in a total amount below 20 wt.%, more preferably in a total amount below 10 wt.%, each based on the total curable fluid weight.

[0079] Fluorinated or silicone compounds are preferably used as a surfactant, however, a potential drawback is bleed-out after image formation because the surfactant does not cross-link. It is therefore preferred to use a copolymerizable monomer having surface-active effects, for example, silicone-modified acrylates, silicone modified methacrylates, fluorinated acrylates, and fluorinated methacrylates.

Colorants

[0080] Colorants may be dyes or pigments or a combination thereof. Organic and/or inorganic pigments may be used.

Suitable dyes include direct dyes, acidic dyes, basic dyes and reactive dyes. Suitable pigments are disclosed in EP-A 1637926 paragraphs [0098] to [0100].

[0081] The pigment is present in the range of 0.01 to 10 wt.%, preferably in the range of 0.1 to 5 wt.%, each based on the total weight of curable fluid.

Solvents

[0082] The curable fluid preferably does not contain an evaporable component, but sometimes, it can be advantageous to incorporate an extremely small amount of a solvent to improve adhesion to the ink-receiver surface after UV curing. In this case, the added solvent may be any amount in the range of 0.1 to 10.0 wt.%, preferably in the range of 0.1 to 5.0 wt.%, each based on the total weight of curable fluid.

Humectants

[0083] When a solvent is used in the curable liquid, a humectant may be added to prevent the clogging of the nozzle, due to its ability to slow down the evaporation rate of curable fluid.

[0084] Suitable humectants are disclosed in EP-A 1637926 paragraph [0105]. A humectant is preferably added to the curable jettable liquid formulation in an amount of 0.01 to 20 wt.% of the formulation, more preferably in an amount of 0.1 to 10 wt.% of the formulation.

Biocides

[0085] Suitable biocides include sodium dihydroacetate, 2-phenoxyethanol, sodium benzoate, sodium pyridinethion-1-oxide, ethyl p-hydroxybenzoate and 1,2-benzisothiazolin-3-one and salts thereof. A preferred biocide is Proxel® GXL available from ZENECA COLOURS.

[0086] A biocide is preferably added in an amount of 0.001 to 3 wt.%, more preferably in an amount of 0.01 to 1.00 wt.%, each based on the total weight of the curable fluid.

Preparation of a curable jettable fluid

[0087] The curable fluids may be prepared as known in the art by mixing or dispersing the ingredients together, optionally followed by milling, as described for example in EP-A 1637322 paragraph [0108]and [0109].

Viscosity of the curable fluids

[0088] As described above, the method according to the present invention may use the aerosol jet printing only, or a combination of aerosol jet printing and inkjet printing.

[0089] The curable fluids to be used for inkjet printing have a viscosity at jetting temperature of less than 15 mPa.s, preferably of less than 12 mPa.s and more preferably of less than 10 mPa.s.

[0090] The curable fluids to be used for aerosol jet printing have a viscosity of less than 5000 mPa.s at jetting temperature, preferably of less than 2500 mPa.s and more preferably of less than 1000 mPa.s.

Flexographic printing support

[0091] Two forms of flexographic printing supports may be used: a plate form and a cylindrical form, the latter commonly referred to as a sleeve. If the print master is created as a plate form, the mounting of the plate form on a printing cylinder may introduce mechanical distortions resulting in so-called anamorphic distortion in the printed image. Such a distortion may be compensated by an anamorphic pre-compensation in an image processing step prior to halftoning.

[0092] Creating the print master directly on a sheet form mounted on a print cylinder or directly on a sleeve avoids the problem of geometric distortion altogether.

[0093] Using a sleeve as support provides improved registration accuracy and faster change over time on press. Furthermore, sleeves may be well-suited for mounting on an inkjet printer having a rotating drum, as shown in Figure 1. This also makes it possible to create seamless flexographic printing sleeves, which have applications in printing continuous designs such as in wallpaper, decoration, gift wrapping paper and packaging.

[0094] The term "flexographic printing support", often encompasses two types of support:

- a support without elastomeric layers on its surface; and
- a support with one or more elastomeric layers on its surface. The one or more elastomeric layers form the so-called

elastomeric floor.

[0095] In the method of the present invention, the flexographic printing support referred to is a support, preferably a sleeve, without one or more elastomeric layers forming an elastomeric floor. Such a sleeve is also referred to as a basic sleeve or a sleeve base. Basic sleeves typically consist of composites, such as epoxy or polyester resins reinforced with glass fibre or carbon fibre mesh. Metals, such as steel, aluminium, copper and nickel, and hard polyurethane surfaces (e.g. durometer 75 Shore D) can also be used. The basic sleeve may be formed from a single layer or multiple layers of flexible material, as for example disclosed by US2002466668. Flexible basic sleeves made of polymeric films can be transparent to ultraviolet radiation and thereby accommodate backflash exposure for building a floor in the cylindrical printing element. Multiple layered basic sleeves may include an adhesive layer or tape between the layers of flexible material. Preferred is a multiple layered basic sleeve as disclosed in US5301610. The basic sleeve may also be made of non-transparent, actinic radiation blocking materials, such as nickel or glass epoxy. The basic sleeve typically has a thickness from 0.1 to 1.5 mm for thin sleeves and from 2 mm to as high as 100 mm for other sleeves. For thick sleeves often combinations of a hard polyurethane surface with a low-density polyurethane foam as an intermediate layer combined with a fibreglass reinforced composite core are used as well as sleeves with a highly compressible surface present on a sleeve base. Depending upon the specific application, sleeve bases may be conical or cylindrical. Cylindrical sleeve bases are used primarily in flexographic printing.

[0096] The basic sleeve or flexographic printing sleeve is stabilized by fitting it over a steel roll core known as an air mandrel or air cylinder. Air mandrels are hollow steel cores which can be pressurized with compressed air through a threaded inlet in the end plate wall. Small holes drilled in the cylindrical wall serve as air outlets. The introduction of air under high pressure permits to float the sleeve into position over an air cushion. Certain thin sleeves are also expanded slightly by the compressed air application, thereby facilitating the gliding movement of the sleeve over the roll core. Foamed adapter or bridge sleeves are used to "bridge" the difference in diameter between the air-cylinder and a flexographic printing sleeve containing the printing relief. The diameter of a sleeve depends upon the required repeat length of the printing job.

Apparatus for creating the flexographic printing master

[0097] Various embodiments of an apparatus for creating the flexographic printing master by the method according to the present invention may be used. In principle a flat bed printing device may be used, for both the inkjet printing and the aerosol jet printing steps, however, a drum based printing device is preferred. A particularly preferred drum based printing device (100) using a sleeve body as flexographic support is shown in Figure 3.

[0098] The sleeve body 130 is mounted on a drum 140. The drum 140 rotates in at a certain speed in the X-direction around axis 110. A printing device 160 moves in the Y-direction. The printing device 160 may be an aerosol jet printing device (module 200 in Figure 1) when only aerosol jet printing is used to prepare the flexographic printing master or a both such an aerosol jet printing device and a conventional inkjet print head when both aerosol jet printing and inkjet printing are used to prepare the flexographic printing master.

[0099] A curing means may be arranged in combination with the printing device, travelling therewith so that the curable fluid is exposed to curing radiation very shortly after been jetted (see Figure 3, curing means 150, printing device 160). It may be difficult to provide a small enough radiation source connected to and travelling with the printing device. Therefore, a static fixed radiation source may be employed, e.g. a source of UV-light, which is then connected to the printing device by means of flexible radiation conductive means such as a fibre optic bundle or an internally reflective flexible tube.

[0100] Alternatively, a source of radiation arranged not to move with the printing device, may be an elongated radiation source extending transversely across the flexographic printing support surface to be cured and parallel with the slow scan direction of the print head (see Figure 3, curing means 170). With such an arrangement, each applied fluid droplet is cured when it passes beneath the curing means 170. The time between jetting and curing depends on the distance between the printhead and the curing means 170 and the rotational speed of the rotating drum 140.

[0101] A combination of both curing means 150 and 170 can also be used as depicted in Figure 3.

Printing device

[0102] The printing device for aerosol jet printing has already been described.

[0103] For inkjet printing, conventional print heads may be used. The means for inkjet printing includes any device capable of coating a surface by breaking up a radiation curable fluid into small droplets which are then directed onto the surface. In the most preferred embodiment the radiation curable fluids are jetted by one or more printing heads ejecting small droplets in a controlled manner through nozzles onto a flexographic printing support, which is moving relative to the printing head(s). A preferred printing head for the inkjet printing system is a piezoelectric head. Piezoelectric inkjet printing is based on the movement of a piezoelectric ceramic transducer when a voltage is applied thereto. The application of a voltage changes the shape of the piezoelectric ceramic transducer in the printing head creating a void, which is then filled with radiation curable fluid. When the voltage is again removed, the ceramic returns to its original shape, ejecting a drop of fluid from the print head. However the inkjet printing method is not restricted to piezoelectric inkjet printing. Other inkjet printing heads can be used and include various types, such as a continuous type and thermal, electrostatic and acoustic drop on demand types. At high printing speeds, the radiation curable fluids must be ejected readily from the printing heads, which puts a number of constraints on the physical properties of the fluid, e.g. a low viscosity at the jetting temperature, which may vary from 25°C to 110°C and a surface energy such that the printing head nozzle can form the necessary small droplets.

[0104] An example of a printhead according to the current invention is capable to eject droplets having a volume between 0.1 and 100 picoliter (pl) and preferably between 1 and 30 pl. Even more preferably the droplet volume is in a range between 1 pl and 8 pl. Even more preferably the droplet volume is only 2 or 3 pl.

[0105] The unpublished EP-A's 10173533.0 and 10173538.9 (both filed 2010-08-20) and 10158421.7 (filed 2010-03-30) preferred constellations of multiple printheads, preferably back to back printheads, are disclosed.

Curing

[0106] Typically for each layer of the relief image, immediately after the deposition of a fluid droplet by the printing device the fluid droplet is exposed by a curing source. This provides immobilization and prevents the droplets to run out, which would deteriorate the quality of the print master. Such curing of applied fluid drops is often referred to as "pinning".

[0107] Curing can be "partial" or "full". The terms "partial curing" and "full curing" refer to the degree of curing, i.e. the percentage of converted functional groups, and may be determined by, for example, RT-FTIR (Real-Time Fourier Transform Infra-Red Spectroscopy) which is a method well known to the one skilled in the art of curable formulations. Partial curing is defined as a degree of curing wherein at least 5 %, preferably 10 %, of the functional groups in the coated formulation or the fluid droplet is converted. Full curing is defined as a degree of curing wherein the increase in the percentage of converted functional groups with increased exposure to radiation (time and/or dose) is negligible. Full curing corresponds with a conversion percentage that is within 10 %, preferably 5 %, from the maximum conversion percentage. The maximum conversion percentage is typically determined by the horizontal asymptote in a graph representing the percentage conversion versus curing energy or curing time. When in the present application the term "no curing" is used, this means that less than 5 %, preferably less than 2.5 %, most preferably less than 1 %, of the functional groups in the coated formulation or the fluid droplet are converted. In the method according to the present invention, applied fluid droplets which are not cured are allowed to spread or coalesce with adjacent applied fluid droplets.

[0108] Curing may be performed by heating (thermal curing), by exposing to actinic radiation (e.g. UV curing) or by electron beam curing. Preferably the curing process is performed by UV radiation.

[0109] The curing means may be arranged in combination with the printing device, travelling therewith so that the curable fluid is exposed to curing radiation very shortly after been jetted (see Figure 3, curing means 150, printing device 160). It may be difficult to provide a small enough radiation source connected to and travelling with the printing device. Therefore, a static fixed radiation source may be employed, e.g. a source of UV-light, which is then connected to the printing device by means of flexible radiation conductive means such as a fibre optic bundle or an internally reflective flexible tube.

[0110] Alternatively, a source of radiation arranged not to move with the printing device, may be an elongated radiation source extending transversely across the flexographic printing support surface to be cured and parallel with the slow scan direction of the print head (see Figure 3, curing means 170). With such an arrangement, each applied fluid droplet is cured when it passes beneath the curing means 170. The time between jetting and curing depends on the distance between the printing device and the curing means 170 and the rotational speed of the rotating drum 140.

[0111] A combination of both curing means 150 and 170 can also be used as depicted in Figure 3.

[0112] Any UV light source, as long as part of the emitted light can be absorbed by the photo-initiator or photo-initiator system of the fluid droplets, may be employed as a radiation source, such as, a high or low pressure mercury lamp, a cold cathode tube, a black light, an ultraviolet LED, an ultraviolet laser, and a flash light. For curing the inkjet printed radiation curable fluid, the imaging apparatus preferably has a plurality of UV light emitting diodes. The advantage of using UV LEDs is that it allows a more compact design of the imaging apparatus.

[0113] UV radiation is generally classified as UV-A, UV-B, and UV-C as follows:

- UV-A: 400 nm to 320 nm
- UV-B: 320 nm to 290 nm
- UV-C: 290 nm to 100 nm

[0114] The most important parameters when selecting a curing source are the spectrum and the intensity of the UV-light. Both parameters affect the speed of the curing. Short wavelength UV radiation, such as UV-C radiation, has poor penetration capabilities and enables to cure droplets primarily on the outside. A typical UV-C light source is low pressure mercury vapour electrical discharge bulb. Such a source has a small spectral distribution of energy, with only a strong peak in the short wavelength region of the UV spectrum.

[0115] Long wavelength UV radiation, such as UV-A radiation, has better penetration properties. A typical UV-A source is a medium or high pressure mercury vapour electrical discharge bulb. Recently UV-LEDs have become commercially available which also emit in the UV-A spectrum and that have the potential to replace gas discharge bulb UV sources. By doping the mercury gas in the discharge bulb with iron or gallium, an emission can be obtained that covers both the UV-A and UV-C spectrum. The intensity of a curing source has a direct effect on curing speed. A high intensity results in higher curing speeds.

[0116] The curing speed should be sufficiently high to avoid oxygen inhibition of free radicals that propagate during curing. Such inhibition not only decreases curing speed, but also negatively affects the conversion ratio of monomer into polymer. To minimize such oxygen inhibition, the imaging apparatus preferably includes one or more oxygen depletion units. The oxygen depletion units place a blanket of nitrogen or other relatively inert gas (e.g. CO_2), with adjustable position and adjustable inert gas concentration, in order to reduce the oxygen concentration in the curing environment. Residual oxygen levels are usually maintained as low as 200 ppm, but are generally in the range of 200 ppm to 1200 ppm.

[0117] Another way to prevent oxygen inhibition is the performance of a low intensity pre-exposure before the actual curing.

[0118] A partially cured fluid droplet is solidified but still contains residual monomer. This approach improves the adhesion properties between the layers that are subsequently printed on top of each other. Partial intermediate curing is possible with UV-C radiation, UV-A radiation or with broad spectrum UV radiation. As mentioned above, UV-C radiation cures the outer skin of a fluid droplet and therefore a UV-C partially cured fluid droplet will have a reduced availability of monomer in the outer skin and this negatively affects the adhesion between neighbouring layers of the relief image. It is therefore preferred to perform the partial curing with UV-A radiation.

[0119] A final post curing however is often realized with UV-C light or with broad spectrum UV light. Final curing with UV-C light has the property that the outside skin of the print master is fully hardened.

Claims

1. A method for preparing a flexographic printing master wherein an optional floor (600), an optional mesa relief (700) and an image relief (800) are applied in this order on a flexographic printing support (1000) by depositing a plurality of layers of a curable fluid on top of each other **characterized in that** at least one layer of a curable fluid is deposited by aerosol jet printing.

2. The method according to claim 1 wherein an upper most layer of the image relief (801) and/or the optional mesa relief (701) and/or the optional floor (601) is applied by aerosol jet printing.

3. The method according to claim 1 or 2 wherein at least one layer of a first curable fluid is applied by aerosol jet printing and wherein at least one layer of a second curable fluid is applied by inkjet printing and wherein the first and the second curable fluid may be the same.

4. The method according to claim 3 wherein the viscosity at depositing temperature of the first curable fluid is higher than the viscosity at depositing temperature of the second curable fluid.

5. The method according to claim 4 wherein the viscosity at depositing temperature of the first curable fluid is higher than 25 mPa.s and wherein said viscosity of the second curable fluid is lower than 15 mPa.s.

6. The method according to any of the preceding claims wherein each layer of a curable fluid is at least partially cured before a subsequent layer of a curable fluid is applied.

7. The method according to any of the preceding claims wherein the flexographic printing support is a sleeve body.

8. The method according to claim 7 wherein the sleeve body comprises a pre-coated floor.

9. An apparatus for carrying out the method as defined in claims 1 to 8 comprising an aerosol jet printing device (160), depositing at least one layer of a curable fluid, and curing means (100 and/or 170).

10. The apparatus according to claim 9 comprising a cylindrical drum (140) on which a sleeve (130) can be mounted.

11. The apparatus according to claim 9 or 10 comprising an aerosol jet printing device depositing a first curable fluid and an inkjet printing device depositing a second curable fluid.

Figure 1: Schematic presentation of Aerosol Jet Printing

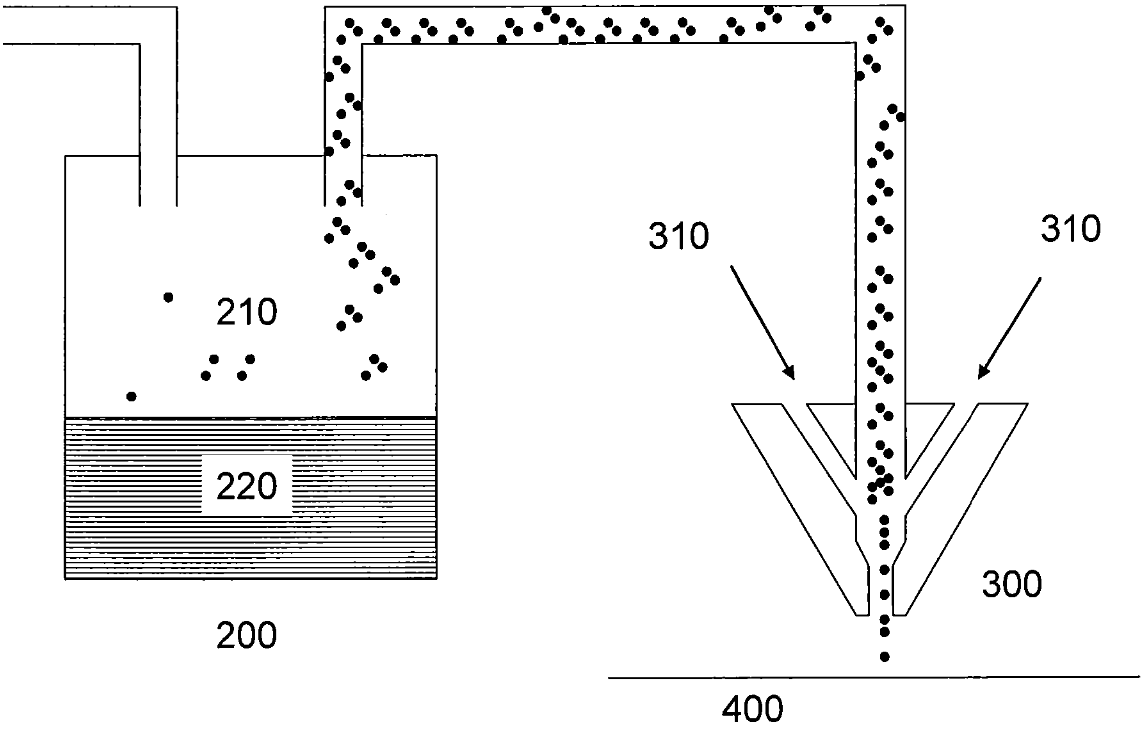


Figure 2: difference between inkjet and aerosol jet printing

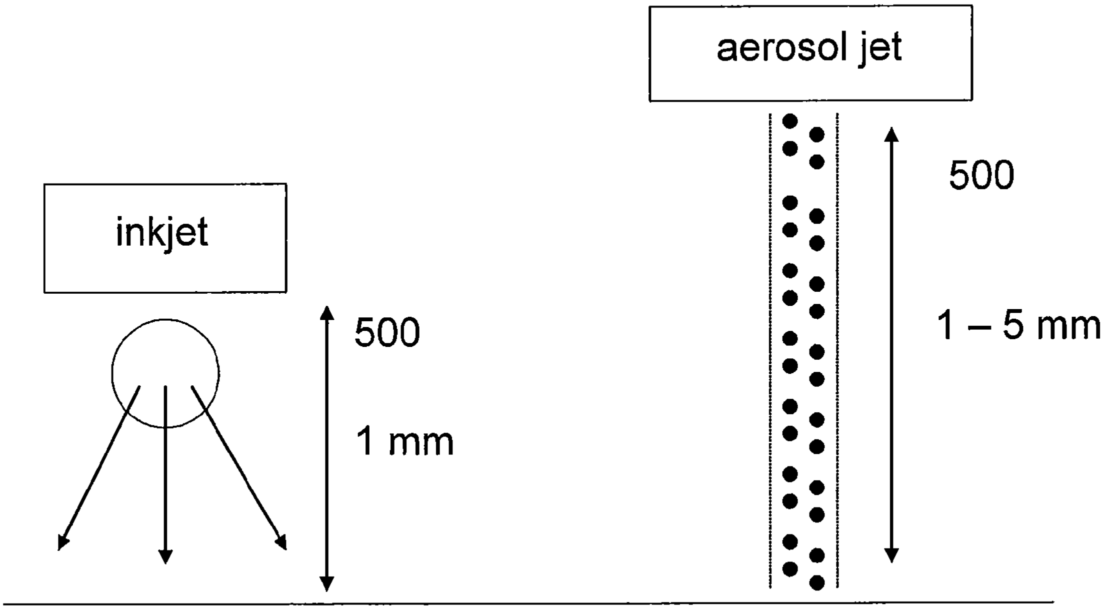


Figure 3

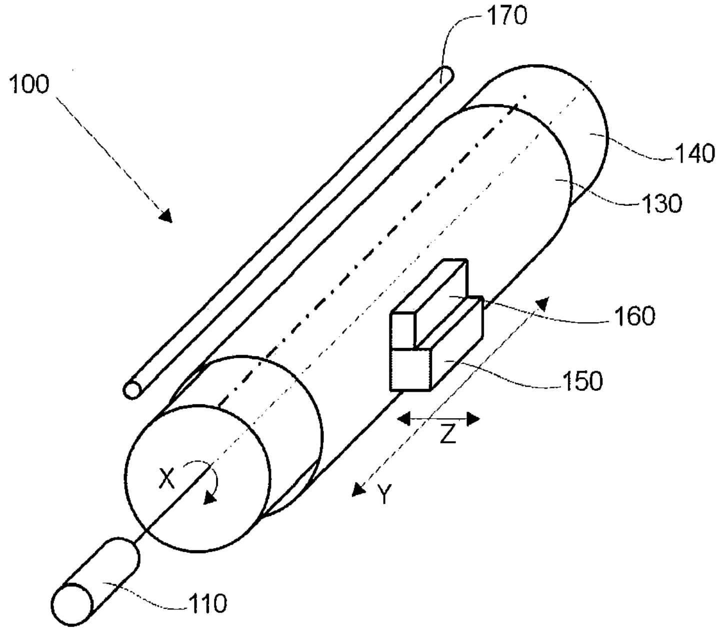
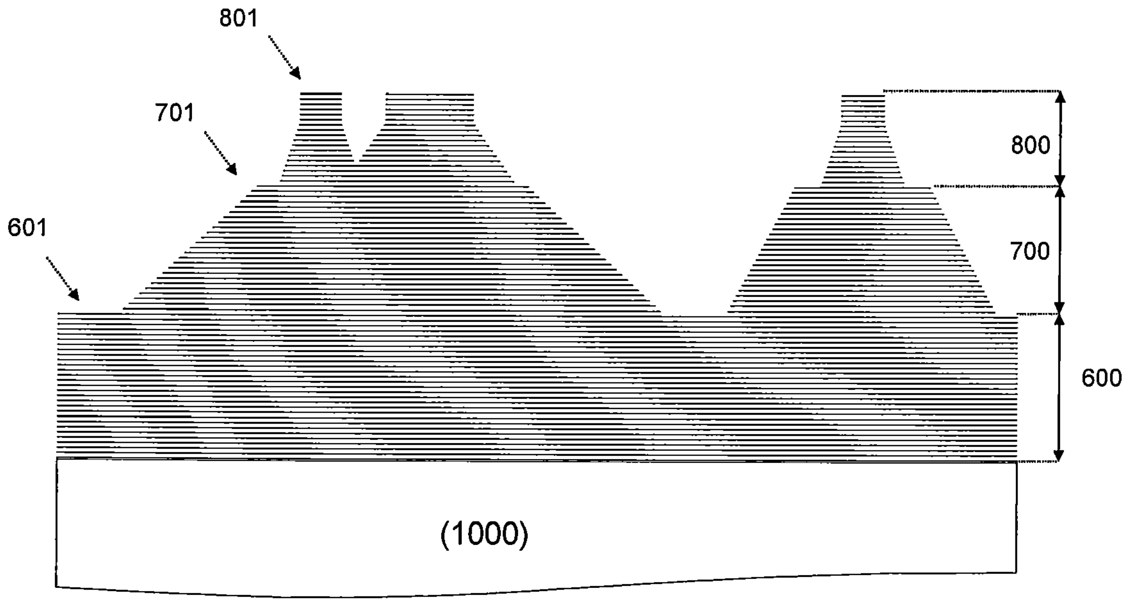


Figure 4



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EUROPEAN SEARCH REPORT

Application Number
EP 11 18 3419

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B41C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	12 March 2012	Giannitsopoulos, G

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2

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