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(54) Title: SOLDER MASK INKJET INKS FOR MANUFACTURING PRINTED CIRCUIT BOARDS

(57) Abstract: The invention provides an inkjet method for producing a solder mask in the manufacture of a Printed Circuit Board. By using a solder mask inkjet ink containing at least one photo-initiator, at least one free radical polymerizable compound and at least one allyl sulfone compound as adhesion promoter, a high quality solder mask withstanding the high thermal stress during the soldering process while maintaining excellent physical properties, may be produced.



Description**Solder Mask Inkjet Inks for Manufacturing Printed Circuit Boards****Technical field of the invention**

[001] The present invention relates to a solder mask inkjet ink and an inkjet method for manufacturing Printed Circuit Boards.

Background art for the invention

[002] Inkjet printing methods have been proposed to further improve the manufacturing process of Printed Circuit Boards (PCBs).

[003] Inkjet printing methods and inkjet inks have been disclosed for legend printing in for example EP-A 2725075 (Agfa) and for applying an etch resist on a copper surface in for example EP-A 2809735 (Agfa) and EP-A 3000853 (Agfa).

[004] By reducing the complexity and minimizing the waste such inkjet printing methods render the manufacture of PCBs more cost effective.

[005] Also for applying the solder mask, inkjet printing methods have been disclosed in for example EP-A 1543704 (Avecia) and EP-A 1624001 (Taiyo Ink Manufacturing).

[006] Solder masks are permanent protective coatings that perform a number of functions during the fabrication, assembly and end use of PCBs. One of the main purposes of solder mask is to protect the circuitry from interacting with solder during the assembly process. A solder mask's job isn't solely restricted to the solder operation however, as it also helps to protect the laminate, holes and traces from collecting contaminants and from degrading during the service life of the PCB. A solder mask also acts as an insulator of known dielectric property between components and traces of the PCB.

[007] UV curable inks are preferred for the design of solder mask inks as they allow a high crosslinking degree, resulting in excellent chemical resistance and mechanical properties. However, compatibility with the high temperature soldering process, while maintaining all physical properties, is especially challenging.

[008] The solder mask inkjet inks disclosed in EP-A 1513704 include an adhesion promoter, which is preferably a (meth)acrylate containing an acid such as for example 2-carboxyethylacrylate.

[009] In EP-A 1624001 the solder mask inkjet ink comprises a monomer having a (meth)acryloyl group and a thermosetting functional group selected from the group consisting of a hydroxyl group, a carboxyl group, an isocyanate group, an amino

group, an imino group, an epoxy group, an oxetanyl group, a mercapto group, a methoxymethyl group, a methoxyethyl group, an ethoxymethyl group, an ethoxyethyl group, and an oxazoline group.

- [010] There is still a need for designing solder mask inkjet inks, which are able to withstand the high thermal stress induced during the soldering process in the manufacture of PCBs.

Summary of the invention

- [011] It is an object of the invention to provide a method for manufacturing a PCB wherein a high quality solder mask, in particular withstanding the high thermal stress during the soldering process while maintaining excellent physical properties, may be produced.
- [012] The object of the invention is realized by the inkjet method according to claim 1.
- [013] Further objects of the invention will become apparent from the description hereinafter.

Detailed description of the invention

Definitions

- [014] The term "monofunctional" in e.g. monofunctional polymerizable compound means that the polymerizable compound includes one polymerizable group.
- [015] The term "difunctional" in e.g. difunctional polymerizable compound means that the polymerizable compound includes two polymerizable groups.
- [016] The term "polyfunctional" in e.g. polyfunctional polymerizable compound means that the polymerizable compound includes more than two polymerizable groups.
- [017] The term "alkyl" means all variants possible for each number of carbon atoms in the alkyl group i.e. methyl, ethyl, for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethylpropyl and 2-methyl-butyl, etc.
- [018] Unless otherwise specified a substituted or unsubstituted alkyl group is preferably a C₁ to C₆-alkyl group.
- [019] Unless otherwise specified a substituted or unsubstituted alkenyl group is preferably a C₂ to C₆-alkenyl group.
- [020] Unless otherwise specified a substituted or unsubstituted alkynyl group is preferably a C₂ to C₆-alkynyl group.
- [021] Unless otherwise specified a substituted or unsubstituted aralkyl group is preferably a phenyl or naphthyl group including one, two, three or more C₁ to C₆-alkyl groups.

- [022] Unless otherwise specified a substituted or unsubstituted alkaryl group is preferably a C₇ to C₂₀-alkyl group including a phenyl group or naphthyl group.
- [023] Unless otherwise specified a substituted or unsubstituted aryl group is preferably a phenyl group or naphthyl group.
- [024] Unless otherwise specified a substituted or unsubstituted heteroaryl group is preferably a five- or six-membered ring substituted by one, two or three oxygen atoms, nitrogen atoms, sulphur atoms, selenium atoms or combinations thereof.
- [025] The term "substituted", in e.g. substituted alkyl group means that the alkyl group may be substituted by other atoms than the atoms normally present in such a group, i.e. carbon and hydrogen. For example, a substituted alkyl group may include a halogen atom or a thiol group. An unsubstituted alkyl group contains only carbon and hydrogen atoms.
- [026] Unless otherwise specified a substituted alkyl group, a substituted alkenyl group, a substituted alkynyl group, a substituted aralkyl group, a substituted alkaryl group, a substituted aryl and a substituted heteroaryl group are preferably substituted by one or more constituents selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tertiary-butyl, ester, amide, ether, thioether, ketone, aldehyde, sulfoxide, sulfone, sulfonate ester, sulphonamide, -Cl, -Br, -I, -OH, -SH, -CN and -NO₂.

Manufacture of an electronic device

- [027] The method of manufacturing an electronic device according to the present invention includes the steps of:
- jetting a radiation curable solder mask inkjet ink as described below on a dielectric substrate containing an electrically conductive pattern; and
 - curing the jetted solder mask inkjet ink.
- [028] The electronic device is preferably a Printed Circuit Board.
- [029] The radiation curable solder mask inkjet ink may be cured by exposing the ink to actinic radiation, such as electron beam or ultraviolet (UV) radiation.
- [030] Preferably the radiation curable inkjet ink is cured by UV radiation, more preferably using UV LED curing.
- [031] The method preferably includes a thermal treatment. The thermal treatment is preferably carried out after the curing step.
- [032] In a preferred embodiment the thermal treatment is carried out at a temperature from 80°C to 250°C. The temperature is preferably not less than 100°C, more preferably not less than 120°C. To prevent charring of the solder mask, the

temperature is preferably not greater than 200°C, more preferably not greater than 160°C.

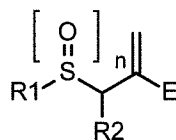
- [033] The thermal treatment is typically carried out between 15 and 90 minutes.
- [034] The purpose of the thermal treatment is to further increase the polymerization degree of the solder mask.
- [035] This further polymerization during the thermal treatment may be accelerated by adding radical initiators which promote thermal curing of polymers, such as peroxides and azo compounds, to the solder mask inkjet ink.
- [036] The dielectric substrate of the electronic device may be any non-conductive material. The substrate is typically a paper/resin composite or a resin/fibre glass composite, a ceramic substrate, a polyester or a polyimide.
- [037] The electrically conductive pattern is typically made from any metal or alloy which is conventionally used for preparing electronic devices such as gold, silver, palladium, nickel/gold, nickel, tin, tin/lead, aluminium, tin/aluminium and copper. The electrically conductive pattern is preferably made from copper.

Radiation curable solder mask inkjet ink

- [038] The radiation curable solder mask inkjet ink comprises at least one photoinitiator, at least one free radical polymerizable compound, and at least one adhesion promoter as disclosed below.
- [039] The solder mask inkjet ink can be cured by e-beam, but is preferably cured by UV light, more preferably by UV light from UV LEDs. The solder mask inkjet ink is thus preferably a UV curable inkjet ink.
- [040] For reliable industrial inkjet printing, the viscosity of the radiation curable inkjet inks is preferably no more than 20 mPa.s at 45°C, more preferably between 1 and 18 mPa.s at 45°C, and most preferably between 4 and 14 mPa.s at 45°C.
- [041] For good image quality and adhesion, the surface tension of the radiation curable inkjet inks is preferably in the range of 18 to 70 mN/m at 25°C, more preferably in the range of 20 to 40 mN/m at 25°C.
- [042] The radiation curable solder mask inkjet ink may further comprise other polymerizable compounds, colorants, polymeric dispersants, a polymerization inhibitor, or a surfactant. The radiation curable solder mask inkjet ink may also comprise a flame retardant.

Adhesion promoter

[043] The adhesion promoter according to the present invention has a structure according to Formula I,



Formula I

wherein

n represents an integer from 0 to 2,

R2 is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl group and a substituted or unsubstituted aryl group,

E is selected from the group consisting of COR10 and a nitrile,

R10 is selected from the group consisting of a hydrogen, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group, OR11 and NR12R13,

R11, R12 and R13 are independently selected from the group consisting of a hydrogen, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group,

R12 and R13 may represent the necessary atoms to form a 5 to 8 membered ring; if n=0,

R1 is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group, R3C=O, R4C=S and R5SO₂,

R3 and R4 are independently selected from the group consisting of a hydrogen, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group, OR6, NR7R8 and SR9,

R5, R6 and R9 are independently selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a

substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group,

R7 and R8 are independently selected from a hydrogen, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group,

R7 and R8 may represent the necessary atoms to form a 5 to 8 membered ring;
If $n=1$ or 2 ,

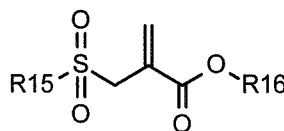
R1 is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group.

[044] In a preferred embodiment R2 represents hydrogen.

[045] In a further preferred embodiment E represents COOR₁₄, wherein R₁₄ is selected from the group consisting of a hydrogen, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group and a substituted or unsubstituted alkyl group optionally substituted in the aliphatic chain by oxygen or nitrogen atoms, oxygen atoms being particularly preferred.

[046] In a further preferred embodiment, n represents 2.

[047] In an even more preferred embodiment the adhesion promoter has a chemical structure according to Formula II,



Formula II

wherein

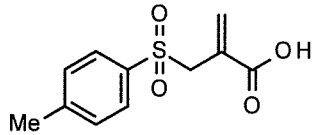
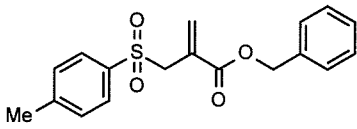
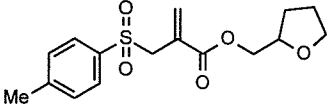
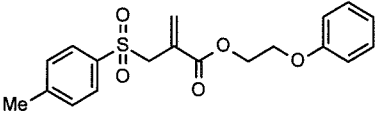
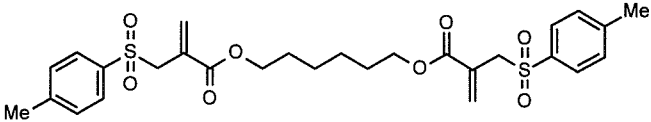
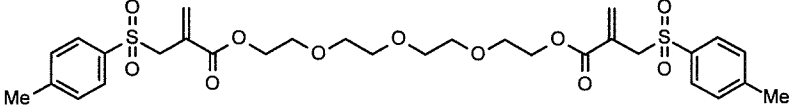
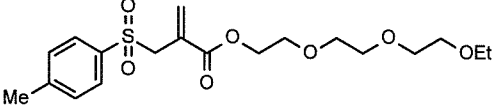
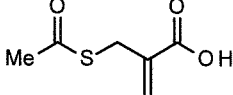
R₁₅ is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or

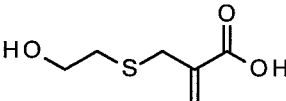
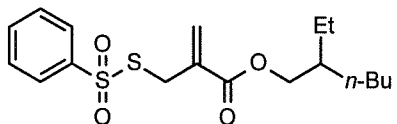
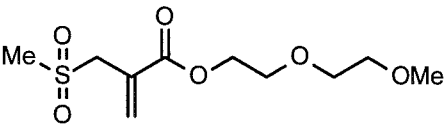
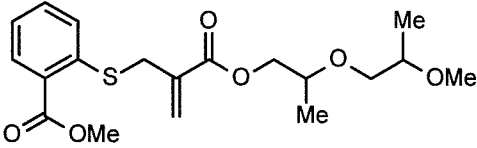
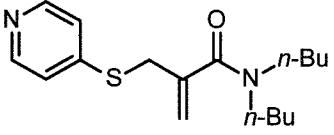
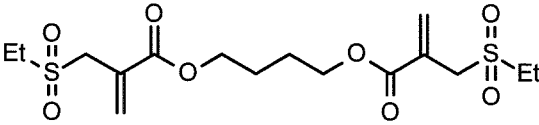
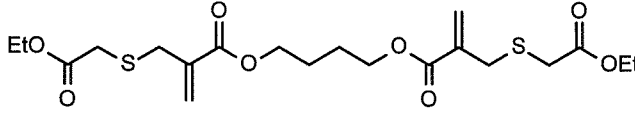
unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group,

R16 is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group.

- [048] In the most preferred embodiment, R16 represents a substituted or unsubstituted alkyl group optionally substituted in the aliphatic chain by oxygen or nitrogen atoms, oxygen atoms being particularly preferred.
- [049] Typical examples of adhesion promoters according to the present invention are given in Table 1 without being limited thereto.

Table 1

	ADH-01
	ADH-02
	ADH-03
	ADH-04
	ADH-05
	ADH-06
	ADH-07
	ADH-08

	ADH-09
	ADH-10
	ADH-11
	ADH-12
	ADH-13
	ADH-14
	ADH-15

[050] The radiation curable solder mask inkjet ink may in addition to the adhesion promoter described above comprise other adhesion promoters, for examples those disclosed in WO2004/028225.

[051] The amount of adhesion promoter in the radiation curable solder mask inkjet ink is preferably between 0.5 and 20 wt%, more preferably between 1 and 15 wt%, most preferably between 2.5 and 10 wt%, relative to the total weight of the inkjet ink.

Free radical polymerizable compounds

[052] The free radical polymerizable compounds may be monomers, oligomers and/or prepolymers.

[053] These monomers, oligomers and/or prepolymers may possess different degrees of functionality. A mixture including combinations of mono-, di-, tri- and higher functional monomers, oligomers and/or prepolymers may be used. The viscosity of the radiation curable inkjet ink may be adjusted by varying the ratio between the monomers and oligomers.

- [054] In a preferred embodiment, the monomer, oligomer or polymer includes at least one acrylate group as polymerizable group.
- [055] Preferred monomers and oligomers are those listed in paragraphs [0106] to [0115] in EP-A 1911814.
- [056] In a preferred embodiment, the radiation curable inkjet ink comprises a monomer containing a vinylether group and an acrylate or methacrylate group. Such monomers are disclosed in EP-A 2848659, paragraphs [0099] to [0104]). A particular preferred monomer containing a vinylether group and an acrylate group is 2-(2-vinyloxyethoxy)ethylacrylate.
- [057] In a particular preferred embodiment, the radiation curable solder mask inkjet ink comprises a free radical polymerizable compound selected from the group consisting of neopentyl-glycol hydroxypivalate diacrylate, isobornyl acrylate, dipropylene glycol diacrylate, trimethylol propane triacrylate, and 2-(vinylethoxy)ethyl acrylate.

Colorants

- [058] The radiation curable solder mask inkjet ink may be a substantially colourless inkjet ink, but preferably the inkjet ink includes at least one colorant.
- [059] The colorant in the solder mask inkjet ink may be a pigment or a dye, but is preferably a pigment.
- [060] A colour pigment may be chosen from those disclosed by HERBST, Willy, et al. Industrial Organic Pigments, Production, Properties, Applications, 3rd edition. Wiley - VCH, 2004, ISBN 3527305769.
- [061] Suitable pigments are disclosed in paragraphs [0128] to [0138] of WO2008/074548.
- [062] Pigment particles in inkjet inks should be sufficiently small to permit free flow of the ink through the inkjet-printing device, especially at the ejecting nozzles. It is also desirable to use small particles for maximum colour strength and to slow down sedimentation. Most preferably, the average pigment particle size is no larger than 150 nm. The average particle size of pigment particles is preferably determined with a Brookhaven Instruments Particle Sizer BI90plus based upon the principle of dynamic light scattering.
- [063] In PCBs, the solder mask typically has a blue or green colour. The blue pigment is preferably one of the phthalocyanine series. Examples of blue pigments are C.I. Pigment Blue 1, 15, 15:1, 15:2, 15:3, 15:4, 15:6, 16, 24 and 60.
- [064] Green pigments are generally a mixture of blue and yellow or orange pigments or may be green pigments per se, such as halogenated phthalocyanines, for example copper or nickel brominated phthalocyanine.

- [065] In a preferred embodiment, the colorant is present in an amount of 0.2 to 6.0 wt%, more preferably 0.5 to 2.5 wt%, based on the total weight of the radiation curable inkjet ink.

Polymeric Dispersants

- [066] If the colorant in the radiation curable solder mask inkjet ink is a pigment, then the radiation curable inkjet preferably contains a dispersant, more preferably a polymeric dispersant, for dispersing the pigment.
- [067] Suitable polymeric dispersants are copolymers of two monomers but they may contain three, four, five or even more monomers. The properties of polymeric dispersants depend on both the nature of the monomers and their distribution in the polymer. Copolymeric dispersants preferably have the following polymer compositions:
- statistically polymerized monomers (e.g. monomers A and B polymerized into ABBAABAB);
 - alternating polymerized monomers (e.g. monomers A and B polymerized into ABABABAB);
 - gradient (tapered) polymerized monomers (e.g. monomers A and B polymerized into AAABAABBABBB);
 - block copolymers (e.g. monomers A and B polymerized into AAAAABBBBBB) wherein the block length of each of the blocks (2, 3, 4, 5 or even more) is important for the dispersion capability of the polymeric dispersant;
 - graft copolymers (graft copolymers consist of a polymeric backbone with polymeric side chains attached to the backbone); and
 - mixed forms of these polymers, e.g. blocky gradient copolymers.
- [068] Suitable polymeric dispersants are listed in the section on "Dispersants", more specifically [0064] to [0070] and [0074] to [0077], in EP-A 1911814.
- [069] Commercial examples of polymeric dispersants are the following:
- DISPERBYK™ dispersants available from BYK CHEMIE GMBH;
 - SOLSPERSE™ dispersants available from NOVEON;
 - TEGO™ DISPERS™ dispersants from EVONIK;
 - EDAPLAN™ dispersants from MÜNZING CHEMIE;
 - ETHACRYL™ dispersants from LYONDELL;
 - GANEX™ dispersants from ISP;
 - DISPEX™ and EFKATM dispersants from CIBA SPECIALTY CHEMICALS INC;
 - DISPONER™ dispersants from DEUCHEM; and
 - JONCRYL™ dispersants from JOHNSON POLYMER.

Photoinitiators and Photoinitiating Systems

- [070] The radiation curable solder mask inkjet ink preferably contains at least one photoinitiator, but may contain a photoinitiating system including a plurality of photoinitiators and/or co-initiators.
- [071] The photoinitiator in the radiation curable inkjet is preferably a free radical initiator, more specifically a Norrish type I initiator or a Norrish type II initiator. A free radical photoinitiator is a chemical compound that initiates polymerization of monomers and oligomers when exposed to actinic radiation by the formation of a free radical. A Norrish Type I initiator is an initiator which cleaves after excitation, yielding the initiating radical immediately. A Norrish type II-initiator is a photoinitiator which is activated by actinic radiation and forms free radicals by hydrogen abstraction from a second compound that becomes the actual initiating free radical. This second compound is called a polymerization synergist or co-initiator. Both type I and type II photoinitiators can be used in the present invention, alone or in combination.
- [072] Suitable photoinitiators are disclosed in CRIVELLO, J.V., et al. Photoinitiators for Free Radical Cationic and Anionic Photopolymerization. 2nd edition. Edited by BRADLEY, G.. London, UK: John Wiley and Sons Ltd, 1998. p.287-294.
- [073] Specific examples of photoinitiators may include, but are not limited to, the following compounds or combinations thereof: benzophenone and substituted benzophenones, 1-hydroxycyclohexyl phenyl ketone, thioxanthenes such as isopropylthioxanthone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2-benzyl-2-dimethylamino- (4-morpholinophenyl) butan-1-one, benzyl dimethylketal, bis (2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide, 2,4,6 trimethylbenzoyl-diphenylphosphine oxide, 2,4,6-trimethoxybenzoyldiphenylphosphine oxide, 2-methyl-1- [4- (methylthio) phenyl] -2-morpholinopropan-1-one, 2,2-dimethoxy-1, 2-diphenylethan-1-one or 5,7-diiodo-3- butoxy-6-fluorone.
- [074] Suitable commercial photoinitiators include Irgacure™ 184, Irgacure™ 500, Irgacure™ 369, Irgacure™ 1700, Irgacure™ 651, Irgacure™ 819, Irgacure™ 1000, Irgacure™ 1300, Irgacure™ 1870, Darocur™ 1173, Darocur™ 2959, Darocur™ 4265 and Darocur™ ITX available from CIBA SPECIALTY CHEMICALS, Lucerin™ TPO available from BASF AG, Esacure™ KT046, Esacure™ KIP150, Esacure™ KT37 and Esacure™ EDB available from LAMBERTI, H-Nu™ 470 and H-Nu™ 470X available from SPECTRA GROUP Ltd..
- [075] The photoinitiator may be a so-called diffusion hindered photoinitiator. A diffusion hindered photoinitiator is a photoinitiator which exhibits a much lower mobility in a cured ink layer than a monofunctional photoinitiator, such as benzophenone.

Several methods can be used to lower the mobility of the photoinitiator. One way is to increase the molecular weight of the photoinitiators so that the diffusion speed is reduced, e.g. polymeric photoinitiators. Another way is to increase its reactivity so that it is built into the polymerizing network, e.g. multifunctional photoinitiators (having 2, 3 or more photoinitiating groups) and polymerizable photoinitiators.

- [076] The diffusion hindered photoinitiator for the radiation curable inkjet is preferably selected from the group consisting of non-polymeric multifunctional photoinitiators, oligomeric or polymeric photoinitiators and polymerizable photoinitiators. Most preferably the diffusion hindered photoinitiator is a polymerizable initiator or a polymeric photoinitiator.
- [077] A preferred diffusion hindered photoinitiator contains one or more photoinitiating functional groups derived from a Norrish type I-photoinitiator selected from the group consisting of benzoinethers, benzil ketals, α,α -dialkoxyacetophenones, α -hydroxyalkylphenones, α -aminoalkylphenones, acylphosphine oxides, acylphosphine sulphides, α -haloketones, α -halosulfones and phenylglyoxalates.
- [078] A preferred diffusion hindered photoinitiator contains one or more photoinitiating functional groups derived from a Norrish type II-initiator selected from the group consisting of benzophenones, thioxanthenes, 1,2-diketones and anthraquinones.
- [079] Suitable diffusion hindered photoinitiators are also those disclosed in EP-A 2065362 in paragraphs [0074] and [0075] for difunctional and multifunctional photoinitiators, in paragraphs [0077] to [0080] for polymeric photoinitiators and in paragraphs [0081] to [0083] for polymerizable photoinitiators.
- [080] A preferred amount of photoinitiator is 0.1 - 20 wt%, more preferably 2 - 15 wt%, and most preferably 3 - 10 wt% of the total weight of the radiation curable inkjet ink.
- [081] In order to increase the photosensitivity further, the radiation curable inkjet may additionally contain co-initiators. Suitable examples of co-initiators can be categorized in three groups: 1) tertiary aliphatic amines such as methyldiethanolamine, dimethylethanolamine, triethanolamine, triethylamine and N-methylmorpholine; (2) aromatic amines such as amylparadimethyl-aminobenzoate, 2-n-butoxyethyl-4-(dimethylamino) benzoate, 2-(dimethylamino)-ethylbenzoate, ethyl-4-(dimethylamino)benzoate, and 2-ethylhexyl-4-(dimethylamino)benzoate; and (3) (meth)acrylated amines such as dialkylamino alkyl(meth)acrylates (e.g., diethylaminoethylacrylate) or N-morpholinoalkyl-(meth)acrylates (e.g., N-morpholinoethyl-acrylate). The preferred co-initiators are aminobenzoates.
- [082] When one or more co-initiators are included into the radiation curable inkjet ink, preferably these co-initiators are diffusion hindered for safety reasons.

- [083] A diffusion hindered co-initiator is preferably selected from the group consisting of non-polymeric di- or multifunctional co-initiators, oligomeric or polymeric co-initiators and polymerizable co-initiators. More preferably the diffusion hindered co-initiator is selected from the group consisting of polymeric co-initiators and polymerizable co-initiators. Most preferably the diffusion hindered co-initiator is a polymerizable co-initiator having at least one (meth)acrylate group, more preferably having at least one acrylate group.
- [084] The radiation curable solder mask inkjet ink preferably includes a polymerizable or polymeric tertiary amine co-initiator.
- [085] Preferred diffusion hindered co-initiators are the polymerizable co-initiators disclosed in EP-A 2053101 in paragraphs [0088] and [0097].
- [086] The radiation curable solder mask inkjet ink preferably includes the (diffusion hindered) co-initiator in an amount of 0.1 to 20 wt%, more preferably in an amount of 0.5 to 15 wt%, most preferably in an amount of 1 to 10 wt% of the total weight of the radiation curable inkjet ink.

Polymerization Inhibitors

- [087] The radiation curable solder mask inkjet ink may contain at least one inhibitor for improving the thermal stability of the ink.
- [088] 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, t-butylcatechol, pyrogallol, 2,6-di-tert.butyl-4-methylphenol (=BHT) may also be used.
- [089] Suitable commercial inhibitors are, for example, Sumilizer™ GA-80, Sumilizer™ GM and Sumilizer™ GS produced by Sumitomo Chemical Co. Ltd.; Genorad™ 16, Genorad™18 and Genorad™ 20 from Rahn AG; Irgastab™UV10 and Irgastab™ UV22, Tinuvin™ 460 and CGS20 from Ciba Specialty Chemicals; Floorstab™ UV range (UV-1, UV-2, UV-5 and UV-8) from Kromachem Ltd, Additol™ S range (S100, S110, S120 and S130) from Cytec Surface Specialties.
- [090] The inhibitor is preferably a polymerizable inhibitor.
- [091] Since excessive addition of these polymerization inhibitors may lower the curing speed, it is preferred that the amount capable of preventing polymerization is determined prior to blending. The amount of a polymerization inhibitor is preferably lower than 5 wt%, more preferably lower than 3 wt% of the total radiation curable inkjet ink.

Surfactants

- [092] The radiation curable solder mask inkjet ink may contain at least one surfactant, but preferably no surfactant is present. If no surfactant is present, the radiation curable inkjet ink does not spread well allowing the generation of thin conductive lines.
- [093] The surfactant can be anionic, cationic, non-ionic, or zwitter-ionic and is usually added in a total quantity less than 1wt% based on the total weight of the radiation curable inkjet ink.
- [094] Suitable surfactants include fluorinated surfactants, fatty acid salts, ester salts of a higher alcohol, alkylbenzene sulfonate salts, sulfosuccinate ester salts and phosphate ester salts of a higher alcohol (for example, sodium dodecylbenzenesulfonate and sodium dioctylsulfosuccinate), ethylene oxide adducts of a higher alcohol, ethylene oxide adducts of an alkylphenol, ethylene oxide adducts of a polyhydric alcohol fatty acid ester, and acetylene glycol and ethylene oxide adducts thereof (for example, polyoxyethylene nonylphenyl ether, and SURFYNOL™ 104, 104H, 440, 465 and TG available from AIR PRODUCTS & CHEMICALS INC.).
- [095] Preferred surfactants are selected from fluoric surfactants (such as fluorinated hydrocarbons) and silicone surfactants. The silicone surfactants are preferably siloxanes and can be alkoxyated, polyether modified, polyether modified hydroxy functional, amine modified, epoxy modified and other modifications or combinations thereof. Preferred siloxanes are polymeric, for example polydimethylsiloxanes.
- [096] Preferred commercial silicone surfactants include BYK™ 333 and BYK™ UV3510 from BYK Chemie.
- [097] In a preferred embodiment, the surfactant is a polymerizable compound.
- [098] Preferred polymerizable silicone surfactants include a (meth)acrylated silicone surfactant. Most preferably the (meth)acrylated silicone surfactant is an acrylated silicone surfactant, because acrylates are more reactive than methacrylates.
- [099] In a preferred embodiment, the (meth)acrylated silicone surfactant is a polyether modified (meth)acrylated polydimethylsiloxane or a polyester modified (meth)acrylated polydimethylsiloxane.
- [0100] Preferably the surfactant is present in the radiation curable inkjet ink in an amount of 0 to 3 wt% based on the total weight of the radiation curable inkjet ink.

Flame retardant

- [0101] The radiation curable solder mask inkjet ink may further contain a flame retardant. In principle all known flame retardants may be used. However, the flame retardant is preferably not a halogen containing compound.
- [0102] Preferred flame retardants are inorganic flame retardants, such as Alumina Trihydrate and Boehmite, and organo-phosphor compounds, such as organo-phosphates (e.g. triphenyl phosphate (TPP), resorcinol bis (diphenylphosphate) (RDP), bisphenol A diphenyl phosphate (BADP), and tricresyl phosphate (TCP)); organo-phosphonates (e.g. dimethyl methylphosphonate (DMMP)); and organo-phosphinates (e.g. aluminium diethyl phosphinate).
- [0103] Other preferred organo-phosphor compounds are disclosed in US8273805.

Preparation of Inkjet Inks

- [0104] The preparation of pigmented radiation curable inkjet inks is well-known to the skilled person. Preferred methods of preparation are disclosed in paragraphs [0076] to [0085] of WO2011/069943.

Inkjet Printing Devices

- [0105] The radiation curable solder mask inkjet ink may be jetted by one or more print heads ejecting small droplets in a controlled manner through nozzles onto a substrate, which is moving relative to the print head(s).
- [0106] A preferred print 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 print head creating a void, which is then filled with ink. When the voltage is again removed, the ceramic expands to its original shape, ejecting a drop of ink from the print head. However the inkjet printing method according to the present invention is not restricted to piezoelectric inkjet printing. Other inkjet print heads can be used and include various types, such as a continuous type.
- [0107] The inkjet print head normally scans back and forth in a transversal direction across the moving ink-receiver surface. Often the inkjet print head does not print on the way back. Bi-directional printing is preferred for obtaining a high areal throughput. Another preferred printing method is by a "single pass printing process", which can be performed by using page wide inkjet print heads or multiple staggered inkjet print heads which cover the entire width of the ink-receiver surface. In a single pass

printing process the inkjet print heads usually remain stationary and the ink-receiver surface is transported under the inkjet print heads.

Curing Devices

- [0108] The radiation curable solder mask inkjet ink can be cured by exposing them to actinic radiation, such as electron beam or ultraviolet radiation. Preferably the radiation curable inkjet ink is cured by ultraviolet radiation, more preferably using UV LED curing.
- [0109] In inkjet printing, the curing means may be arranged in combination with the print head of the inkjet printer, travelling therewith so that the curable liquid is exposed to curing radiation very shortly after been jetted.
- [0110] In such an arrangement, with the exception of UV LEDs, it can be difficult to provide a small enough radiation source connected to and travelling with the print head. Therefore, a static fixed radiation source may be employed, e.g. a source of curing UV-light, connected to the radiation source by means of flexible radiation conductive means such as a fibre optic bundle or an internally reflective flexible tube.
- [0111] Alternatively, the actinic radiation may be supplied from a fixed source to the radiation head by an arrangement of mirrors including a mirror upon the radiation head.
- [0112] The source of radiation may also be an elongated radiation source extending transversely across the substrate to be cured. It may be adjacent the transverse path of the print head so that the subsequent rows of images formed by the print head are passed, stepwise or continually, beneath that radiation source.
- [0113] Any ultraviolet light source, as long as part of the emitted light can be absorbed by the photo-initiator or photo-initiator system, 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. Of these, the preferred source is one exhibiting a relatively long wavelength UV-contribution having a dominant wavelength of 300-400 nm. Specifically, a UV-A light source is preferred due to the reduced light scattering therewith resulting in more efficient interior curing.
- [0114] UV radiation is generally classed 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.
- [0115] In a preferred embodiment, the radiation curable inkjet ink is cured by UV LEDs. The inkjet printing device preferably contains one or more UV LEDs preferably with a wavelength larger than 360 nm, preferably one or more UV LEDs with a wavelength

larger than 380 nm, and most preferably UV LEDs with a wavelength of about 395 nm.

- [0116] Furthermore, it is possible to cure the ink image using, consecutively or simultaneously, two light sources of differing wavelength or illuminance. For example, the first UV-source can be selected to be rich in UV-C, in particular in the range of 260 nm-200 nm. The second UV-source can then be rich in UV-A, e.g. a gallium-doped lamp, or a different lamp high in both UV-A and UV-B. The use of two UV-sources has been found to have advantages e.g. a fast curing speed and a high curing degree.
- [0117] For facilitating curing, the inkjet printing device often includes one or more oxygen depletion units. The oxygen depletion units place a blanket of nitrogen or other relatively inert gas (e.g. CO₂), 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.

EXAMPLES

Materials

- [0118] All materials used in the following examples were readily available from standard sources such as ALDRICH CHEMICAL Co. (Belgium) and ACROS (Belgium) unless otherwise specified. The water used was deionized water.
- [0119] **SR606A** is neopentylglycol hydroxypivalate diacrylate available as Sartomer™ SR606A from ARKEMA.
- [0120] **ACMO** is acryloyl morpholine available from RAHN.
- [0121] **ITX** is Speedcure™ ITX, a mixture of isopropyl thioxanthone isomers, from LAMBSON SPECIALTY CHEMICALS.
- [0122] **TPO** is 2,4,6-trimethylbenzoyldiphenylphosphine oxide, supplied by RAHN AG
- [0123] **EPD** is ethyl-4-(dimethylamino)benzoate, available under the trade name of Genocure™ EPD from RAHN AG.
- [0124] **BAPO** is a bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide photoinitiator available as Irgacure™ 819 from BASF.
- [0125] **CN146** is (2-acryloyloxyethyl) phthalate from ARKEMA.
- [0126] **INHIB** is a mixture forming a polymerization inhibitor having a composition according to Table 2.

Table 2

Component	wt%
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DPGDA	82.4
p-methoxyphenol	4.0
2,6-di-tert-butyl-4-methylphenol	10.0
Cupferron™ AL	3.6

- [0127] Cupferron™ AL is aluminum N-nitrosophenylhydroxylamine from WAKO CHEMICALS LTD.
- [0128] Ebecryl 1360 AK is a polysiloxane hexa acrylate slip agent from ALLNEX.
- [0129] IBOA is isobornylacrylate, available as Sartomer™ 506D from SARTOMER.
- [0130] DPGDA is dipropylenediacylate, available as Sartomer SR508 from SARTOMER.
- [0131] TMPTA is trimethylol propane triacrylate, available as Sartomer™ SR351 from SARTOMER.
- [0132] FST426R is a difunctional urethane methacrylate from CLARIANT.
- [0133] VEEA is 2-(vinylethoxy)ethyl acrylate available from NIPPON SHOKUBAI, Japan.
- [0134] Cyan is SUN FAST BLUE 15:4, a cyan pigment available from SUN CHEMICALS.
- [0135] Yellow is CROMOPHTAL YELLOW D 1085J, a yellow pigment from BASF.
- [0136] Disperbyk 162 is a dispersing agent and has been precipitated from a solution available from BYK (ALTANA).

Methods

Coatings/prints of the solder mask inkjet inks

- [0137] To evaluate the adhesion and the solder resistance of the solder mask inkjet inks, the inks were coated on a brushed copper foil (35 μ) at a coating thickness of 20 μ and cured using a H-bulb (1 pass at 20 m/min). Additionally, the coatings were thermally cured at 150°C during 30 minutes.

Evaluation solder resistance

- [0138] The solder resistance of the solder mask inkjet inks was evaluated using a SPL600240 Digital Dynamic Solder Pot available from L&M PRODUCTS filled with a "K" Grade 63:37 tin/lead solder available from SOLDER CONNECTION. The temperature of the solder was set at 290°C.
- [0139] Using a Q-tip, a solder flux SC7560A from SOLDER CONNECTION was applied on the surface of the samples (i.e. coatings of the solder mask inkjet ink on a copper surface) to clean the surface. The solder flux was dried by placing the samples for 10 minutes above the solder pot.

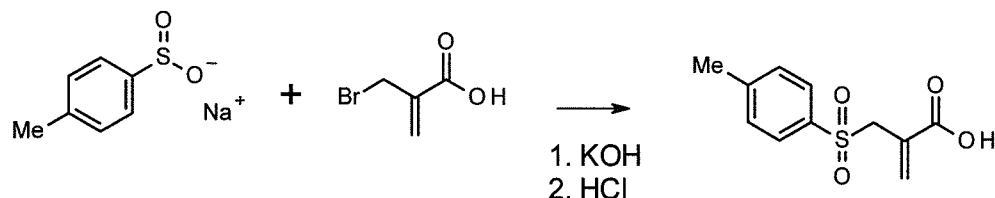
- [0140] After placing the sample in the solder pot, a solder wave was created for 10 seconds after which the samples were cooled for at least 10 minutes.
- [0141] The adhesion of the solder mask inkjet inks on the copper surface was then evaluated with a tape test on the cooled samples. A black tape Tesa 4104/04 from TESA AG, Germany was taped onto the coating and the tape was removed immediately thereafter by hand.
- [0142] A visual evaluation resulted in an adhesion quality ranging from 0 (very good adhesion) to 5 (very poor adhesion).

Viscosity

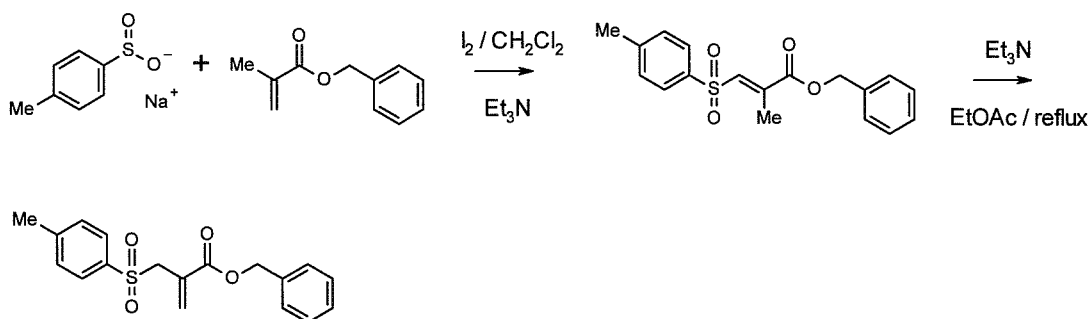
- [0143] The viscosity of the inks was measured at 45°C and at a shear rate of 1 000 s⁻¹ using a "Robotic Viscometer Type VISCObot" from CAMBRIDGE APPLIED SYSTEMS.
- [0144] For industrial inkjet printing, the viscosity at 45°C and at a shear rate of 1000 s⁻¹ is preferably between 3 and 20 mPa.s. More preferably the viscosity at 45°C and at a shear rate of 1000 s⁻¹ is less than 15 mPa.s.

Preparation of the adhesion promoters

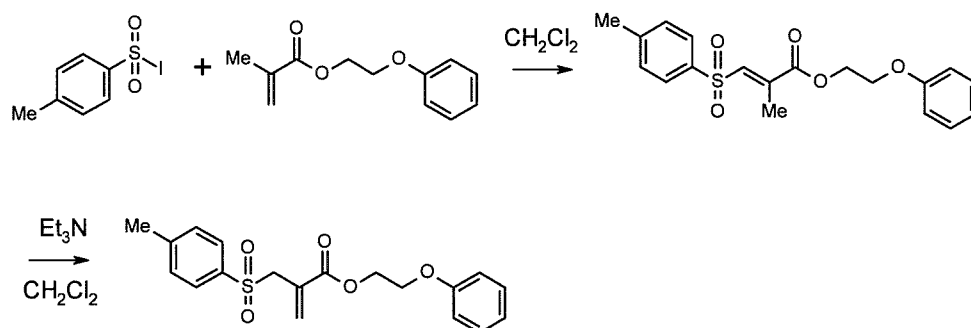
The synthesis of ADH-1



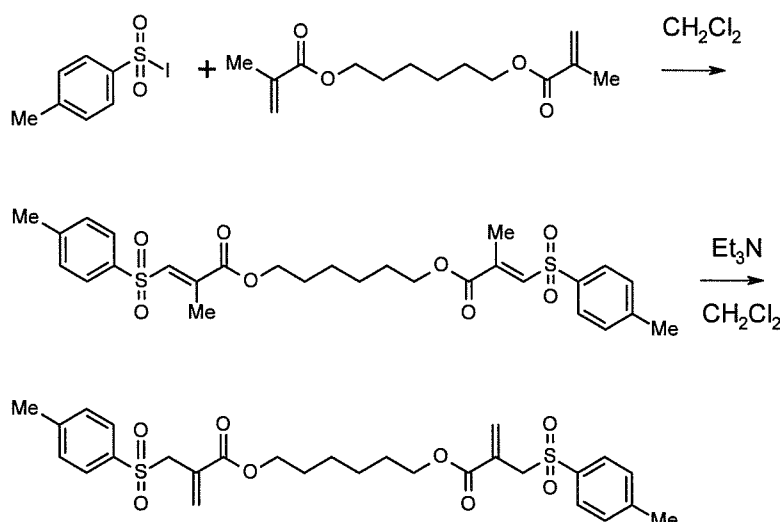
- [0145] 2.3 g (14 mmol) of 2-(bromomethyl)-2-propenoic acid was dissolved in 30 ml methanol. After the addition of 0.8 g (14 mmol) potassium hydroxide the mixture was stirred for 15 minutes. Then, 2.5 g (14 mmol) tolyl sulfinic acid sodium salt was added to the mixture and the reaction was allowed to continue for 16 hours at room temperature. After removal of the solvent under reduced pressure, the residue was dissolved in 200 ml of a 2N sodium hydroxide solution. The mixture was extracted with 100 ml methyl *t*-butyl ether. The aqueous fraction was isolated and cooled to 0°C. After the addition of a 6N hydrochloric acid solution, ADH-1 precipitated from the medium. ADH-1 was then isolated by filtration, washed with 100 ml water and dried.
- [0146] 2.4 g (yield = 71%) of ADH-1 was obtained. ADH-1 was analyzed using ¹H-NMR spectroscopy (DMSO-d₆, 2.4 ppm (3H); 4.28 ppm (2H); 5.73 ppm (1H), 6.28 ppm (1H); 7.42 ppm (2H); 7.67 ppm (2H)).

The synthesis of ADH-2

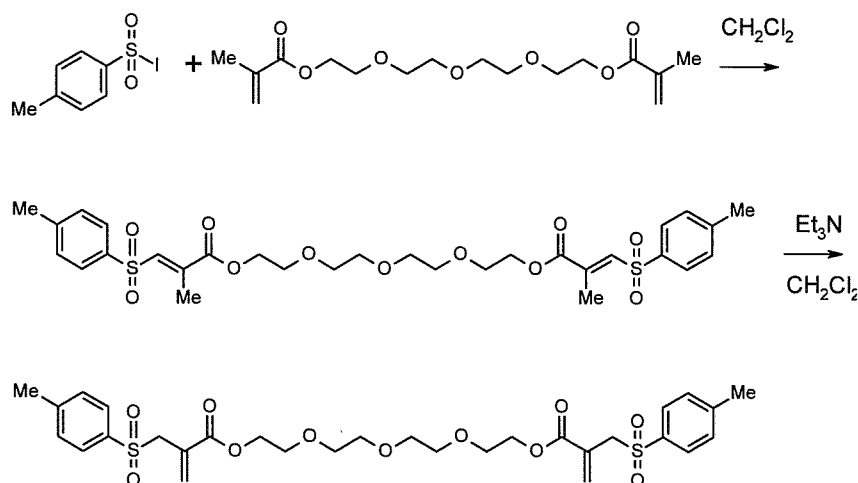
- [0147] 52.8 g (0.3 mol) benzyl methacrylate was dissolved in 400 ml methylene chloride. Then, 53.4 g (0.3 mol) of the sodium salt of tolyl sulfinic acid was added followed by the addition of 76.1 g (0.3 mol) iodine. The reaction was allowed to continue at room temperature for 24 hours. After extracting the mixture three times with 500 ml of a 3 wt% solution of sodium thiosulfate, the organic fraction was isolated, dried over MgSO_4 and evaporated under reduced pressure. After dissolving the residue in 150 ml methylene chloride, 112 ml (80.64 g, 0.8 mol) triethyl amine was dropwise added. The reaction was allowed to continue for 16 hours followed by the removal of the solvent under reduced pressure. The residue was treated with 250 ml methanol and the intermediate product precipitated from the medium. The intermediate product was isolated by filtration and dried. 25.4 g of the intermediate product was isolated and used in the next step without further purification.
- [0148] 25 g (76 mmol) of the intermediate product was added to 100 ml ethyl acetate followed by the addition of 11 ml (7.92 g, 78 mmol) triethyl amine. The reaction mixture was then refluxed for 5 hours, after which it was allowed to cool down to room temperature. ADH-2 crystallized from the medium upon standing and was isolated by filtration.
- [0149] 14 g (yield = 14% overall) of ADH-2 was obtained. ADH-2 was analyzed using ^1H -NMR spectroscopy (DMSO-d_6 , 2.4 ppm, s (3H); 4.36 ppm, m (2H); 5.04 ppm, s (2H); 5.83, m (1H); 6.4 ppm, m (1H); 7.38 ppm, m (7H); 7.66 ppm, m (2H)).

The synthesis of ADH-4

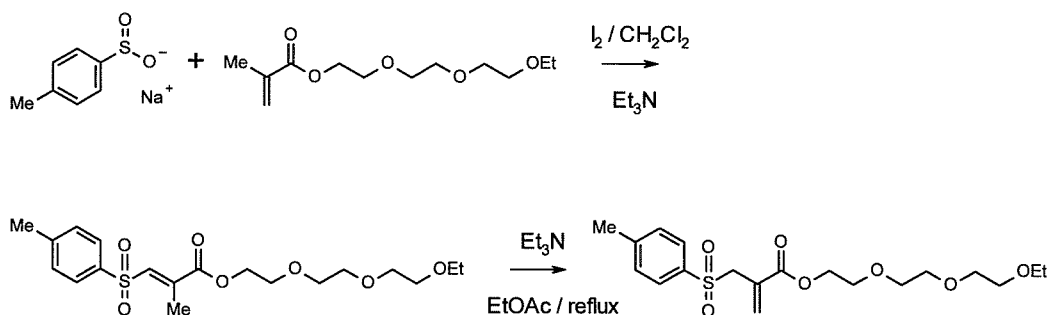
- [0150] 7.1 g (25 mmol) p-toluene sulfonyl iodide was dissolved in 70 ml methylene chloride. After the addition of a solution of 5.1 g (25 mmol) phenyl methacrylate in 10 ml methylene chloride, the reaction mixture was exposed to a 250 W infrared lamp, supplied by Philips, at 10 cm distance from the reaction vessel. The reaction was allowed to continue for two hours at room temperature under continuous exposure. After completion of the reaction, the mixture was extracted twice with 50 ml of a 5 wt% solution of Na₂S₂O₄ and three times with 100 ml water. The organic fraction was dried over MgSO₄ and evaporated under reduced pressure. The residue was dissolved in 70 ml methylene chloride and cooled to 0°C. A solution of 7.6 g (75 mmol) triethyl amine in 10 ml methylene chloride was added and the reaction was allowed to continue for 24 hours at room temperature. The reaction mixture was extracted twice with 50 ml of a 1N hydrochloric acid solution and twice with 50 ml water. The organic fraction was isolated, dried over MgSO₄ and evaporated under reduced pressure. The crude ADH-4 was purified by preparative column chromatography on a Prochrom LC80 column using Kromasil Si 60A 10μ as stationary phase and methylene chloride / ethyl acetate 98 / 2 as eluent.
- [0151] 4.75 g (yield = 52 %) of ADH-4 was isolated (TLC analysis on TLC Silica gel 60F254, supplied by Merck, methylene chloride/ ethyl acetate 98/2, R_f : 0.31).
- [0152] ADH-4 was analyzed using ¹H-NMR spectroscopy (DMSO-d₆, 2.35 (3H); 4.15 (2H); 4.27 (2H); 4.33 ppm (2H); 5.83 ppm (1H); 6.34 ppm (1H); 6.93 ppm (3H); 7.3 ppm (2H); 7.4 ppm (2H); 7.66 ppm (2H)).

The synthesis of ADH-5

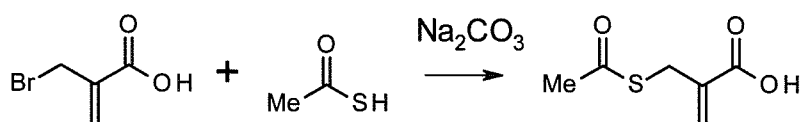
- [0153] 6.2 g (22 mmol) *p*-toluene sulfonyl iodide was dissolved in 30 ml methylene chloride. A solution of 2.5 g (10 mmol) hexane diol dimethacrylate in 30 ml methylene chloride was added. The reaction was allowed to continue for 90 minutes at room temperature. The reaction mixture was extracted twice with 50 ml of a 5w% solution of Na₂S₂O₄ solution and three times with 100 ml water. The organic fraction was dried over MgSO₄. The MgSO₄ was removed by filtration and the filtrate was cooled to 0°C. A solution of 3 g (30 mmol) triethyl amine in 30 ml methylene chloride was added and the reaction was allowed to continue for 24 hours at room temperature. An additional 3 g (30 mmol) of triethyl amine was added and the reaction was allowed to continue for 72 hours at room temperature. The reaction mixture was extracted twice with 100 ml of a 1N hydrochloric acid solution and three times with 100 ml water. The organic fraction was dried over MgSO₄ and evaporated under reduced pressure. The crude ADH-5 was purified by preparative column chromatography on a GraceResolve column using a gradient elution from methylene chloride to methylene chloride/ethyl acetate 95/5 (TLC analysis on TLC Silica gel 60F254, supplied by Merck, methylene chloride/ethyl acetate 94/6, R_f: 0.25).
- [0154] 2.4 g (yield = 42 %) of ADH-5 was obtained. ADH-5 was analyzed using ¹H-NMR spectroscopy (DMSO-d₆, 1.22 ppm (4H); 1.49 ppm (4H); 2.32 ppm (6H); 3.91 ppm (4H); 4.26 ppm (4H); 5.74 ppm (2H); 6.28 ppm (2H); 7.37 ppm (4H); 7.60 ppm (2H)).

The synthesis of ADH-6

- [0155] 6.2 g (22 mmol) *p*-toluene sulfonyl iodide was dissolved in 30 ml methylene chloride. A solution of 3.3 g (10 mmol) tetraethylene glycol dimethacrylate was added and the reaction mixture was exposed to a 250 W infrared lamp, supplied by Philips at 10 cm distance from the reaction vessel. The reaction was allowed to continue for four hours at room temperature under continuous exposure. After completion of the reaction, the mixture was extracted twice with 50 ml of a 5wt% solution of Na₂S₂O₄ solution. The aqueous fraction was extracted with 20 ml methylene chloride and the pooled methylene chloride fractions were extracted with 50 ml of a 5wt% solution of Na₂S₂O₄ and twice with 100 ml water. The organic fraction was dried over MgSO₄. The MgSO₄ was removed by filtration and 3 g (30 mmol) triethyl amine in 30 ml methylene chloride was added to the filtrate. The reaction was allowed to continue for 16 hours at room temperature followed by an extra addition of 3 g (30 mmol) triethyl amine. The reaction was allowed to continue at room temperature for an additional 24 hours. 100 ml of a 1 N hydrochloric acid solution was added to the mixture. The organic fraction was isolated and extracted with 100 ml of a 1 N hydrochloric acid solution and twice with 100 ml water. The organic fraction was dried over MgSO₄ and evaporated under reduced pressure. The crude ADH-6 was purified using preparative column chromatography on a Prochrom LC80 column using Kromasil Si 60A 10μ as stationary phase and a gradient elution from methylene chloride to methylene chloride / ethyl acetate 65/35 as eluent.
- [0156] 2.5 g (yield = 39 %) of ADH-6 was isolated (TLC analysis on TLC Silica gel 60F254, supplied by Merck, methylene chloride/ methanol 97/3, R_f : 0.25).
- [0157] ADH-6 was analyzed using ¹H-NMR spectroscopy (DMSO-d₆, 2.4 ppm (6H); 3.57 ppm (12 H); 4.07 ppm (4H); 4.3 ppm (4H); 5.81 ppm (2H); 6.34 ppm (2H); 7.43 ppm (4H), 7.68 ppm (4H)).

The synthesis of ADH-7

- [0158] 35.6 g (0.2 mol) tolyl sulfinic acid sodium salt was added to 200 ml methylene chloride. 86.1 g (0.35 mol) ethoxy-ethoxy-ethoxy-ethyl methacrylate was added followed by the addition of 76 g (0.3 mol) iodine. The reaction was allowed to continue for 24 hours at room temperature. The mixture was extracted twice with 250 ml of a 6wt% solution of sodium thiosulfate. The organic fraction was isolated and dried over MgSO_4 . The MgSO_4 was removed by filtration and 60.6 g (0.6 mol) triethyl amine was added to the filtrate. The reaction was allowed to continue for 16 hours at room temperature. The solvent was removed under reduced pressure and the residue was redissolved in 300 ml acetone. One liter of a 1/1 mixture of hexane and isopropyl acetate was added to the solution and the precipitated salts were removed by filtration. The solvent was evaporated under reduced pressure and the residue was redissolved in 300 ml ethyl acetate. 56.56 g triethyl amine was added at room temperature over 30 minutes. The reaction mixture was refluxed for 6 hours. The mixture was allowed to cool down to room temperature and was extracted three times with 100 ml 2 N hydrochloric acid. The organic fraction was isolated, dried over MgSO_4 and evaporated under reduced pressure. The crude ADH-7 was purified by preparative column chromatography on a Prochrom LC80 column using Kromsil Si 60A 10 μ as stationary phase and ethyl acetate / hexane 70/30 as eluent.
- [0159] 30 g (yield = 37.5 %) of ADH-7 was isolated. (TLC analysis on TLC Silica gel 60F254, supplied by Merck, ethyl acetate/ hexane 70/30, R_f : 0.6).
- [0160] ADH-7 was analyzed using ^1H -NMR spectroscopy (CDCl_3 , 1.12 ppm (3H); 2.43 ppm (3H); 3.57 ppm (2H); 3.61 ppm (2H); 3.68 ppm (8H); 4.18 ppm (4H); 5.92 ppm (1H); 6.53 ppm (1H); 7.38 ppm (2H); 7.75 ppm (2H))

The synthesis of ADH-8

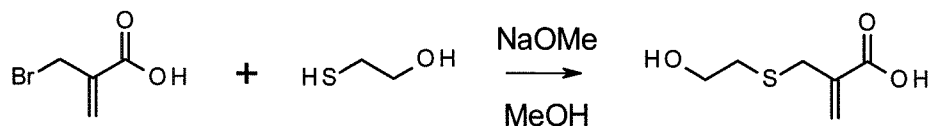
- [0161] 10 g (60.6 mmol) 2-(bromomethyl)-2-propenoic acid was suspended in 200 ml water. 10.9 g (103 mmol) sodium carbonate in 40 ml water was added to the

suspension followed by the addition of 5.07 g (66.7 mmol) thioacetic acid. The reaction was allowed to continue for 25 minutes at room temperature after which the reaction mixture was acidified to pH = 1 using 5 N HCl. The mixture was then extracted with 200 ml ethyl acetate. The solvent was removed under reduced pressure and ADH-8 was isolated as a white solid.

[0162] ADH-8 was analyzed using LCMS using a HP1100 Esquire HCT Ultra spectrometer in combination with an Alltech Alltima C18 column (150 x 3, 5 μ m). A flow rate of 0.5 ml/min was used at 40°C. An isocratic elution using a 10 mmol formic acid solution in water for five minutes followed by a gradient elution from a 10 mmol formic acid solution in water to a 10 mmol formic acid solution in acetonitrile over 25 minutes was used.

[0163] A sample of 3 mg of ADH-8 in 20 ml water acetonitrile 1/1 was prepared. 5 μ l of this solution was injected. ADH-8 had 99.4% purity based on area percentages.

The synthesis of ADH-9



[0164] 17.3 g (0.105 mol) of 2-(bromomethyl)-2-propenoic acid was dissolved in 50 ml methanol. The mixture was cooled to 10 °C and 38.9 ml of a 30 wt% sodium methanolate solution in methanol was added while maintaining the temperature below 15°C. A solution of 7.8 g (0.1 mol) 2-mercapto-ethanol in 50 ml methanol was added while maintaining the temperature below 20°C. The reaction was allowed to continue for one hour at room temperature. The precipitated salts were removed by filtration and the solvent was removed under reduced pressure. The residue was redissolved in 100 ml water and acidified with 50 ml of a 5N hydrochloric acid solution. The mixture was extracted twice with 200 ml ethyl acetate. The pooled ethyl acetate fractions were washed twice with 200 ml water. All aqueous fractions were pooled and extracted twice with 200 ml ethyl acetate. The pooled ethyl acetate fractions were dried over MgSO₄ and evaporated under reduced pressure. The crude ADH-9 was purified using preparative column chromatography on a Prochrom LC80 column using Kromasil Si 60A 10 μ as stationary phase and methylene chloride / ethanol 93 / 7 as eluent.

[0165] 2.0 g (yield = 12%) of ADH-9 was isolated (TLC analysis POLYGRAM SIL G/UV₂₅₄, methylene chloride / ethanol 93/7, R_f : 0.33).

[0166] ADH-9 was analyzed using ^1H -NMR spectroscopy (DMSO- d_6 , 2.47 ppm (2H); 3.33 ppm (2H); 3.53 ppm (2H); 5.63 ppm (1H), 6.03 ppm (1H)).

Preparation of the Cyan and Yellow pigment dispersions CPD and YPD

[0167] Concentrated Cyan and Yellow and pigment dispersions, respectively CPD and YPD, were prepared having a composition according to Table 3.

Table 3

wt% of:	CPD	YPD
Cyan	15	-
Yellow	-	15
Disperbyk 162	15	=
INHIB	1	=
VEEA	69	=

[0168] CPD and YPD were prepared as follows: 138 g of 2-(2-vinyloxyethoxy)ethyl acrylate, 2 g of a solution containing 4 wt% of 4-methoxyphenol, 10 wt% of 2,6-Di-tert-butyl-4-methylphenol and 3.6 wt% of Aluminum-N-nitroso phenylhydroxyl amine in dipropylene glycol diacrylate, 200 g of a 30 wt% solution of Disperbyk 162 in 2-(2-Vinyloxyethoxy)ethyl acrylate and 60 g of Cyan (for CPD) or 60 g of Yellow (for YPD) were mixed using a DISPERLUX™ dispenser. Stirring was continued for 30 minutes. The vessel was connected to a NETZSCH MiniZeta mill filled with 900 g of 0.4 mm yttrium stabilized zirconia beads ("high wear resistant zirconia grinding media" from TOSOH Co.). The mixture was circulated over the mill for 120 minutes (residence time of 45 minutes) and a rotation speed in the mill of about 10.4 m/s. During the complete milling procedure the content in the mill was cooled to keep the temperature below 60°C. After milling, the dispersion was discharged into a vessel.

[0169] The resulting concentrated pigment dispersions CPD and YPD exhibited an average particle size of respectively 80 nm and 131 nm, as measured with a Malvern™ nano-S, and a viscosity of respectively 51 mPa.s and 114 mPa.s at 25°C and at a shear rate of 10 s⁻¹.

Example 1

[0170] This example illustrates the superior solder mask resistance of UV curable inkjet inks including adhesion promoters according to the present invention.

Preparation of comparative ink COMP-1 and inventive inks INV-1 to INV-7

[0171] The comparative radiation curable inkjet ink COMP-1 and the inventive radiation curable inkjet ink INV-1 to INV-7 were prepared according to Table 4. The weight percentages (wt%) are all based on the total weight of the radiation curable inkjet ink.

Table 4

wt% of component	COMP-1	INV-1	INV-2	INV-3	INV-4	INV-5	INV-6	INV-7
CPD	6.65	=	=	=	=	=	=	=
YPD	6.65	=	=	=	=	=	=	=
IBOA	25.00	20.00	=	=	=	=	=	=
DPGDA	22.75	=	=	=	=	=	=	=
TMPTA	20.00	=	=	=	=	=	=	=
FST426R	5.00	=	=	=	=	=	=	=
ITX	4.00	=	=	=	=	=	=	=
TPO	2.95	=	=	=	=	=	=	=
EPD	4.00	=	=	=	=	=	=	=
BAPO	2.00	=	=	=	=	=	=	=
ADH-01	-	5.00	-	-	-	-	-	-
ADH-02	-	-	5.00	-	-	-	-	-
ADH-04	-	-		5.00	-	-	-	-
ADH-06	-	-	-	-	5.00	-	-	-
ADH-07	-	-	-	-	-	5.00	-	-
ADH-08	-	-	-	-	-	-	5.00	-
ADH-09	-	-	-	-	-	-	-	5.00
Ebecryl 1360 AK	0.10	=	=	=	=	=	=	=
INHIB	0.90	=	=	=	=	=	=	=

[0172] The solder resistance of the comparative ink COMP-01 and the inventive inks INV-1 to INV-7 were tested as described above. The results are shown in Table 5.

Table 5

UV curable ink jet ink	Solder Resistance
COMP-1	5

INV-1	0
INV-2	0
INV-3	1
INV-4	0
INV-5	1
INV-6	0
INV-7	1

[0173] It is clear from the results of Table 5 that the inventive solder mask inkjet inks containing an adhesion promoter according to the present invention all have a superior solder resistance compared to a solder mask inkjet ink without such an adhesion promoter.

Example 2

[0174] This example illustrates the superior solder mask resistance of UV curable inkjet inks including adhesion promoters according to the present invention.

Preparation of comparative ink COMP-2 and inventive inks INV-8 to INV-14

[0175] The comparative radiation curable inkjet ink COMP-2 and the inventive radiation curable inkjet ink INV-8 to INV-14 were prepared according to Table 6. The weight percentages (wt%) are all based on the total weight of the radiation curable inkjet ink.

Table 6

wt% of component	COMP-2	INV-8	INV-9	INV-10	INV-11	INV-12	INV-13	INV-14
CPD	6.65	=	=	=	=	=	=	=
YPD	6.65	=	=	=	=	=	=	=
TMPTA	5.00	=	=	=	=	=	=	=
SR606 A	33.00	=	=	=	=	=	=	=
VEEA	36.45	31.45	=	=	=	=	=	=
ITX	4.00	=	=	=	=	=	=	=
TPO	2.95	=	=	=	=	=	=	=
EPD	4.00	=	=	=	=	=	=	=
ADH-01	-	5.00	-	-	-	-	-	-
ADH-04	-	-	5.00	-	-	-	-	-

ADH-05	-	-	-	5.00	-	-	-	-
ADH-06	-	-	-	-	5.00	-	-	-
ADH-07	-	-	-	-	-	5.00	-	-
ADH-08	-	-	-	-	-	-	5.00	-
ADH-09	-	-	-	-	-	-	-	5.00
Ebecryl 1360 AK	0.10	=	=	=	=	=	=	=
INHIB	0.90	=	=	=	=	=	=	=

[0176] The solder resistance of the comparative ink COMP-02 and the inventive inks INV-8 to INV-14 were tested as described above. The results are shown in Table 7.

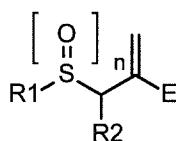
Table 7

UV curable ink jet ink	Solder Resistance
COMP-2	5
INV-8	1
INV-9	0
INV-10	1
INV-11	0
INV-12	0
INV-13	0
INV-14	0

[0177] It is clear from the results of Table 7 that the inventive solder mask inkjet inks containing an adhesion promoter according to the present invention all have a superior solder resistance compared to a solder mask inkjet ink without such an adhesion promoter.

Claims

1. A method of manufacturing an electronic device including the steps of:
- jetting a radiation curable solder mask inkjet ink to a dielectric substrate containing an electrically conductive pattern; and
 - curing the jetted solder mask inkjet;
- characterized in that the solder mask inkjet ink comprises a photoinitiator, a free radical polymerizable compound, and an adhesion promoter according to Formula I,



Formula I

wherein

n represents an integer from 0 to 2,

R2 is selected from the group consisting of a hydrogen atom, a substituted or unsubstituted alkyl group and a substituted or unsubstituted aryl group,

E is selected from the group consisting of COR10 and a nitrile,

R10 is selected from the group consisting of a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group, OR11 and NR12R13,

R11, R12 and R13 are independently selected from the group consisting of a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group,

R12 and R13 may represent the necessary atoms to form a 5 to 8 membered ring, if n=0;

R1 is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group, R3C=O, R4C=S and R5SO₂,

R3 and R4 are independently selected from the group consisting of a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl

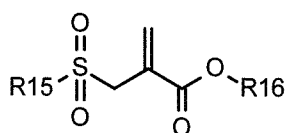
group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group, OR6, NR7R8 and SR9, R5, R6 and R9 are independently selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group,

R7 and R8 are independently selected from a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group,

R7 and R8 may represent the necessary atoms to form a 5 to 8 membered ring, If $n=1$ or 2,

R1 is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group.

2. The method according to claim 1 wherein R2 represents a hydrogen atom.
3. The method according to claim 1 or 2 wherein E represents COOR14 and wherein R14 is selected from the group consisting of a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group, a substituted or unsubstituted aryl group or heteroaryl group, and a substituted or unsubstituted alkyl group optionally substituted in the aliphatic chain by oxygen or nitrogen atoms.
4. The method according to any of the preceding claims wherein n represents 2.
5. The method according to any of the preceding claims wherein the adhesion promoter has a chemical structure according to Formula II,



Formula II

wherein

R15 is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group,

R16 is selected from the group consisting of a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted alkaryl group and a substituted or unsubstituted aryl group or heteroaryl group.

6. The method according to claim 5 wherein R16 represents a substituted or unsubstituted alkyl group optionally substituted in the aliphatic chain by oxygen or nitrogen atoms.
7. The method according to any of the preceding claims wherein the amount of the adhesion promoter is between 0.5 and 20 wt%, relative to the total weight of the solder mask inkjet ink.
8. The method according to any of the preceding claims wherein the free radical polymerizable compound is selected from the group consisting of neopentyl glycol hydroxypivalate diacrylate, isobornyl acrylate, dipropylene glycol diacrylate, trimethylol propane triacrylate, and 2-(vinylethoxy)ethyl acrylate.
9. The method according to any of the preceding claims wherein the radiation curable solder mask inkjet ink further comprises a cyan, yellow or green pigment.
10. The method according to any of the preceding claims wherein curing is carried out using UV radiation.
11. The method according to any of the preceding claims wherein the curing is carried out using UV LED radiation.
12. The method according to any of the preceding claims also comprising a heating step.
13. The method according to claim 12 wherein the heating step is carried out at a temperature between 80°C and 250°C.
14. The method according to any of the preceding claims wherein the electrically conductive pattern is a copper pattern.
15. The method according to any of the preceding claims wherein the electronic device is a Printed Circuit Board.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/078406

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/101 B41M5/00 C09D11/322 C09D11/38 H05K1/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D B41M H05K

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/028225 A1 (AVECIA LTD [GB]; HOPPER ALAN JOHN [GB]; JAMES MARK ROBERT [GB]) 1 April 2004 (2004-04-01) cited in the application page 4, line 39 - page 6, line 14 table 1 claims 1-30 ----- -/--	1-15



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 application or patent 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

30 November 2017

Date of mailing of the international search report

08/12/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Inzenhofer, Kathrin

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/078406

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PAUL GAUSS ET AL: "The influence of vinyl activating groups on [beta]-allyl sulfone-based chain transfer agents for tough methacrylate networks", JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY, vol. 54, no. 10, 17 December 2015 (2015-12-17), pages 1417-1427, XP055360914, ISSN: 0887-624X, DOI: 10.1002/pola.27993 [retrieved on 2017-03-31] figure 1 Testing of CTAs in Monofunctional Model Formulation; page 1421, column 2 - page 1422, column 2; table 1 CONCLUSIONS; page 1426 -----	1-15
A	SAMUEL CLARK LIGON ET AL: "Allyl sulfides and [alpha]-substituted acrylates as addition-fragmentation chain transfer agents for methacrylate polymer networks", JOURNAL OF POLYMER SCIENCE, PART A: POLYMER CHEMISTRY, vol. 54, no. 3, 17 August 2015 (2015-08-17), pages 394-406, XP055360917, ISSN: 0887-624X, DOI: 10.1002/pola.27788 [retrieved on 2017-03-31] figure 1 Photoreactivity of Allyl Sulfide CTAs; page 397, column 2 - page 398, column 1 CONCLUSIONS; page 405, column 2 - column 3 -----	1-15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2017/078406

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.: 1-15(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.: 1-15(partially)

Due to severe deficiencies regarding disclosure of the invention (see Item VII) and clarity (see Item VIII), it is - at present - not possible to provide a full assessment regarding novelty and inventive step. However, clear and sufficiently disclosed exemplary embodiments of the invention (tables 4 and 6) have been searched.

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 Guidelines C-IV, 7.2), 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/EP2017/078406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004028225	A1	01-04-2004	AT 326828 T 15-06-2006
		AU 2003260739 A1 08-04-2004	
		CN 1695407 A 09-11-2005	
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		EP 1543704 A1 22-06-2005	
		JP 2005539390 A 22-12-2005	
		KR 20050057461 A 16-06-2005	
		TW I318231 B 11-12-2009	
		US 2006047014 A1 02-03-2006	
		WO 2004028225 A1 01-04-2004	
