(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 November 2014 (27.11.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/188209 A1

(51) International Patent Classification:
C09D 11/10 (2014.01) *C09D 11/00* (2014.01)

(21) International Application Number:
PCT/GB2014/051588

(22) International Filing Date:
23 May 2014 (23.05.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1309432.1 24 May 2013 (24.05.2013) GB

(71) Applicant: **SERICOL LIMITED** [GB/GB]; PO Box Patricia Way, Pysons Road Industrial Estate, Broadstairs, Kent CT10 2LE (GB).

(72) Inventors: **WARD, Jeremy**; c/o Sericol Limited, PO Box Patricia Way, Pysons Road Industrial Estate, Broadstairs, Kent CT10 2LE (GB). **GOULD, Nigel**; c/o Sericol Limited, PO Box Patricia Way, Pysons Road Industrial Estate, Broadstairs, Kent CT10 2LE (GB). **TURNER, James**; c/o Sericol Limited, PO Box Patricia Way, Pysons Road Industrial Estate, Broadstairs Kent CT10 2LE (GB).

(74) Agent: **ELKINGTON AND FIFE LLP**; Thavies Inn House, 3-4 Holborn Circus, London EC1N 2HA (GB).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *with amended claims (Art. 19(1))*

WO 2014/188209 A1

(54) Title: PRINTING INK

(57) Abstract: The present invention provides a hybrid inkjet ink comprising: (i) at least 30% by weight of an organic solvent based on the total weight of the ink; (ii) a radiation-curable oligomer and/or a radiation-curable multifunctional monomers; (iii) a photoinitiator; (iv) optionally a colorant; and (v) 8-25% by weight, based on the total weight of the ink, of a passive thermoplastic resin having a weight-average molecular weight of 1,500 to 70,000.

Printing ink

The present invention relates to a printing ink, and particularly to an ink for printing onto PET containers, such as PET bottles.

Inkjet printing is an attractive technique for printing onto a wide-range of substrates on account of its flexibility and ease of use. However, PET containers represent a particular challenge. The principle of printing an ink directly onto such a container is superficially attractive as it would streamline the process, but adhesion of the ink to the containers represents a serious challenge.

For this reason, the approach presently taken in the art is to use pre-printed (paper) labels which were then stuck onto the PET containers using an adhesive.

There is therefore a need in the art for an inkjet ink which can be printed directly onto PET containers.

Accordingly, the present invention provides a hybrid inkjet ink comprising: (i) at least 30% by weight of an organic solvent based on the total weight of the ink; (ii) a radiation-curable oligomer and/or a radiation-curable multifunctional monomer; (iii) a photoinitiator; (iv) optionally a colorant; and (v) 8-25% by weight, based on the total weight of the ink, of a passive thermoplastic resin having a weight-average molecular weight of 1,500 to 70,000.

It has surprisingly been found that the combination of the radiation-curable material and passive thermoplastic resin together with the organic solvent provides an ink which has the necessary adhesion to PET containers, whilst maintaining a sufficiently low viscosity for inkjet printing.

The ink of the present invention comprises a modified ink binder system. The presence of a radiation-curable material, a passive thermoplastic resin and a photoinitiator in the ink means that crosslinked polymers can be formed in the dried ink film, leading to improved adhesion to PET containers and improved resistance to solvents. The presence of at least 30% by weight of organic solvent means that the advantageous properties of solvent-based inkjet inks are maintained.

By “radiation-curable” is meant a material that polymerises or crosslinks when exposed to actinic radiation, commonly ultraviolet light, in the presence of a photoinitiator.

The radiation-curable material includes one or more radiation-curable oligomers and/or one or more radiation-curable multifunctional monomers. The monomers/oligomers may possess different degrees of functionality.

Radiation-curable oligomers suitable for use in the present invention comprise a backbone, for example a polyester, urethane, epoxy or polyether backbone, and one or more radiation polymerisable groups. The oligomer preferably comprises a urethane backbone. The polymerisable group can be any group that is capable of polymerising upon exposure to radiation. Preferably the oligomers are multifunctional, more preferably have a functionality of 2-6. Preferably the oligomers are (meth)acrylate oligomers.

Particularly preferred radiation-curable materials are urethane acrylate oligomers as these have excellent adhesion and elongation properties. Most preferred are tri-, tetra-, penta- or hexa-functional urethane acrylates, particularly hexafunctional urethane acrylates as these yield films with good solvent resistance.

Other suitable examples of radiation-curable oligomers include epoxy based materials such as bisphenol A epoxy acrylates and epoxy novolac acrylates, which have fast cure speeds and provide cured films with good solvent resistance.

Preferred oligomers have a molecular weight of 600 to 4,000. Molecular weights (number average) can be calculated if the structure of the oligomer is known or molecular weights can be measured using gel permeation chromatography using polystyrene standards.

In a preferred embodiment the radiation-curable oligomer polymerises by free-radical polymerisation.

The radiation-curable oligomer used in the ink of the invention cures upon exposure to radiation in the presence of a photoinitiator to form a crosslinked, solid film. The resulting film has good adhesion to substrates and good solvent resistance. Any radiation-curable oligomer that is compatible with the remaining ink components and that is capable of curing to form a crosslinked, solid film is suitable for use in the ink of the present invention. Thus, the ink formulator is able to select from a wide range of suitable oligomers. In particular, the oligomer can be a low molecular weight material that is in liquid form at 25°C. This is beneficial when aiming to produce a low viscosity ink. Furthermore, the use of a low molecular weight, liquid oligomer is advantageous when formulating the ink because low molecular weight liquid oligomers are likely to be miscible in a wide range of solvents.

Radiation-curable multifunctional monomers suitable for use in the present invention typically have a molecular weight of less than 600. They preferably have a functionality of 3-6, e.g. tri-

and tetra-, penta- and hexafunctional monomers. They include multifunctional (meth)acrylate monomers, Examples of the multifunctional acrylate monomers that may be included in the ink-jet inks include hexanediol diacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyethylene glycol diacrylate (for example tetraethylene glycol diacrylate), dipropylene glycol diacrylate, tri(propylene glycol) triacrylate, neopentyl glycol diacrylate, bis(pentaerythritol) hexaacrylate, and the acrylate esters of ethoxylated or propoxylated glycols and polyols, for example, propoxylated neopentyl glycol diacrylate, ethoxylated trimethylolpropane triacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate (DPHA), ethoxylated pentaerythritol tetraacrylate and mixtures thereof. Dipentaerythritol hexaacrylate (DPHA) is particularly preferred.

Suitable multifunctional (meth)acrylate monomers also include esters of methacrylic acid (i.e. methacrylates), such as hexanediol dimethacrylate, trimethylolpropane trimethacrylate, triethyleneglycol dimethacrylate, diethyleneglycol dimethacrylate, ethyleneglycol dimethacrylate, 1,4-butanediol dimethacrylate. Mixtures of (meth)acrylates may also be used.

The total amount of the radiation-curable oligomer and radiation-curable multifunctional monomer present in the ink is preferably 5 to 30% by weight based on the total weight of the ink, more preferably 5 to 20% by weight, and most preferably 5 to 15% by weight.

The ink of the present invention is typically used for packaging food and drink. Therefore, it is beneficial for the ink to be substantially free of migrateable monofunctional monomers, including (meth)acrylates, α,β-unsaturated ethers and vinyl amides. Accordingly, the present invention preferably contains less than 5% by weight of monofunctional monomers, more preferably less than 2% by weight and most preferably less than 1% by weight, based on the total weight of the ink

Typical monofunctional (meth)acrylate monomers to be excluded are phenoxyethyl acrylate (PEA), cyclic TMP formal acrylate (CTFA), isobornyl acrylate (IBOA), tetrahydrofurfuryl acrylate (THFA), 2-(2-ethoxyethoxy)ethyl acrylate, octadecyl acrylate (ODA), tridecyl acrylate (TDA), isodecyl acrylate (IDA) and lauryl acrylate. Typical N-vinyl amides and N-(meth)acryloyl amines to be excluded are N-vinyl caprolactam (NVC), N-vinyl pyrrolidone (NVP) and N-acryloylmorpholine (ACMO).

(Meth)acrylate is intended herein to have its standard meaning, i.e. acrylate and/or methacrylate. Mono and multifunctional are also intended to have their standard meanings, i.e. one and two or more groups, respectively, which take part in the polymerisation reaction on curing.

In an alternative embodiment of the invention, the radiation-curable material is capable of polymerising by cationic polymerisation. Suitable materials include, oxetanes, cycloaliphatic epoxides, bisphenol A epoxides, epoxy novolacs and the like. The radiation-curable material according to this embodiment may comprise a mixture of cationically curable monomer and oligomer. For example, the radiation-curable material may comprise a mixture of an epoxide oligomer and an oxetane monomer. The radiation-curable material can also comprise a combination of free-radical polymerisable and cationically polymerisable materials.

The ink of the invention includes one or more photoinitiators. When the ink of the invention includes a free-radical polymerisable material the photoinitiator system includes a free-radical photoinitiator and when the inks include a cationic polymerisable material the photoinitiator system includes a cationic photoinitiator. When the inks comprise a combination of free-radical polymerisable and cationically polymerisable materials both a free-radical and cationic initiator are required. The ink is preferably free-radical polymerisable.

The free-radical photoinitiator can be selected from any of those known in the art. For example, benzophenone, 1-hydroxycyclohexyl phenyl ketone, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one, 2-benzyl-2-dimethylamino-(4-morpholinophenyl)butan-1-one, isopropyl thioxanthone, benzil dimethylketal, bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide or mixtures thereof. Such photoinitiators are known and commercially available such as, for example, under the trade names Irgacure and Darocur (from Ciba) and Lucerin (from BASF).

In one embodiment, the ink of the present invention may be formulated to comply with regulations for printing onto secondary food packaging. For compositions designed specifically for use on food packaging it is essential that they meet regulations regarding migrateable materials. For these applications it is desirable to use photoinitiators allowed by legislation and guidance (e.g. EuPIA Inventory List 2012, Nestle Guidance Notes).

Non limiting examples of allowed photoinitiators include 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)butan-1-one (Irgacure 379), bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819), 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) and polymeric photoinitiators such as polymeric ITX or polymeric benzophenone for example Speedcure 7010 (polymeric ITX from Lambsons) and Genopol BP-2 (polymeric benzophenone from Rahn).

In the case of a cationically curable system, any suitable cationic initiator can be used, for example sulfonium or iodonium based systems. Non limiting examples include Esacure 1064 and Esacure 1187 from Lamberti, Irgacure 250, Irgacure 270 and Irgacure 290 from BASF, Uvacure 1600 from Cytec and, Speedcure 992 and Speedcure 976 from Lambsons.

Preferably the photoinitiator is present in an amount of 1 to 20% by weight, preferably 3 to 10% by weight, based on the total weight of the ink.

The ink also contains a passive (or "inert") thermoplastic resin. Passive resins are resins which do not enter into the curing process, i.e. the resin is free of functional groups which polymerise under the curing conditions to which the ink is exposed. In other words, resin is not a radiation-curable material. The resin may be selected from epoxy, polyester, vinyl, ketone, nitrocellulose, phenoxy or acrylate resins, or a mixture thereof and is preferably a polyester resin.

The passive thermoplastic resin has a weight-average molecular weight (Mw) of 1,500 to 70,000. Preferably the molecular weight is 2,000 or more, more preferably 3,000 or more, more preferably 4,000 or more and most preferably 5,000 or more; and 30,000 or less, more preferably 20,000 or less, more preferably 15,000 or less and most preferably 10,000 or less. The Mw may be measured by known techniques in the art, such a gel permeation chromatography (GPC).

A suitable GPC apparatus for measuring Mw is an LC instrument having the following parameters - Column set: MiniMix E or MiniMix D (depending on molecular weight), Eluent: THF, Detector: UV/vis and/or ELS, Calibration: conventional vs polystyrene. This approach is applicable to polymers having a Mw of 400-400,000.

The resin also preferably has a melting point range falling within the range of 30 to 150ºC.

A particularly preferred resin is LTH resin from Evonik. This resin has a viscosity of 600-1,500 mPas at 23ºC in 60% xylene, a Mn of 2,766, a Mw of 5,717 and a melting point of 90-102ºC.

The resin is present at 8-25% by weight, preferably 10-20% by weight, based on the total weight of the ink.

It has been found that the combination of the oligomer and/or multifunctional monomer and the passive thermoplastic resin provide the necessary binding properties to the substrate after the ink has cured/dried to a solid film, whilst providing an appropriate viscosity for jetting and providing the required printed film properties and necessary stability to the ink suspension on storage, i.e. prior to jetting.

The ink of the invention contains an organic solvent. The organic solvent is in the form of a liquid at ambient temperatures and is capable of acting as a carrier for the remaining components of the ink. The organic solvent component of the ink may be a single solvent or

a mixture of two or more solvents. As with known solvent-based inkjet inks, the organic solvent used in the ink of the present invention is required to evaporate from the printed ink, typically on heating, in order to allow the ink to dry. The solvent can be selected from any solvent commonly used in the printing industry, such as glycol ethers, glycol ether esters, alcohols, ketones, esters, organic carbonates, lactones and pyrrolidones.

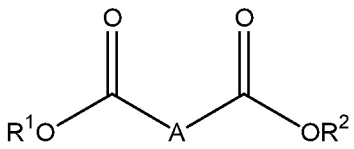
The organic solvent is present in an amount of at least 30% by weight, preferably at least 50% by weight, and most preferably at least 60% by weight based on the total weight of the ink. The upper limit is typically 85% or 75% by weight based on the total weight of the ink.

In a preferred embodiment the organic solvent is a low toxicity and/or a low odour solvent. Solvents that have been given VOC exempt status by the United States Environmental Protection Agency or European Council are also preferred.

The most preferred solvents are selected from alcohols, glycol ethers, glycol ether acetates, lactones and mixtures thereof.

In another embodiment of the invention, dibasic esters and/or bio-solvents may be used.

Dibasic esters are known solvents in the art. They can be described as di(C_1-C_4 alkyl) esters of a saturated aliphatic dicarboxylic acid having 3 to 8 carbon atoms having following general formula:



in which A represents $(CH_2)_{1-6}$, and R^1 and R^2 may be the same or different and represent C_1-C_4 alkyl which may be a linear or branched alkyl radical having 1 to 4 carbon atoms, preferably methyl or ethyl, and most preferably methyl. Mixtures of dibasic esters can be used.

Bio-solvents, or solvent replacements from biological sources, have the potential to reduce dramatically the amount of environmentally-polluting VOCs released in to the atmosphere and have the further advantage that they are sustainable. Moreover, new methods of production of bio-solvents derived from biological feedstocks are being discovered, which allow bio-solvent production at lower cost and higher purity.

Examples of bio-solvents include soy methyl ester, lactate esters, polyhydroxyalkanoates, terpenes and non-linear alcohols, and D-limonene. Soy methyl ester is prepared from soy.

The fatty acid ester is produced by esterification of soy oil with methanol. Lactate esters preferably use fermentation-derived lactic acid which is reacted with methanol and/or ethanol to produce the ester. An example is ethyl lactate which is derived from corn (a renewable source) and is approved by the FDA for use as a food additive. Polyhydroxyalkanoates are linear polyesters which are derived from fermentation of sugars or lipids. Terpenes and non-linear alcohols may be derived from corn cobs/rice hulls. An example is D-limonene which may be extracted from citrus rinds.

Other solvents may be included in the organic solvent component. A particularly common source of other solvents is derived from the way in which the colouring agent is introduced into the inkjet ink formulation. The colouring agent may be prepared in the form of a pigment dispersion in a solvent, e.g. 2-ethylhexyl acetate. The solvent tends to be around 40 to 50% by weight of the pigment dispersion based on the total weight of the pigment dispersion and the pigment dispersion typically makes up around 5 to 15% by weight of the ink and sometimes more.

The ink is preferably substantially free of water, although some water will typically be absorbed by the ink from the air or be present as impurities in the components of the inks, and such levels are tolerated. For example, the ink may comprise less than 5% by weight of water, more preferably less than 2% by weight of water and most preferably less than 1% by weight of water, based on the total weight of the ink.

The ink of the present invention may be a coloured or a colourless ink. By “colourless” is meant that the ink is free of colorant such that no colour can be detected by the naked eye. Minor amounts of colorant that do not produce colour that can be detected by the eye can be tolerated, however. Typically the amount of colorant present will be less than 0.3% by weight based on the total weight of the ink, preferably less than 0.1%, more preferably less than 0.03%. Colourless inks may also be described as “clear” or “water white”. Colourless inks may also be used as a varnish, where it is applied over a coloured ink. For the avoidance of doubt, coloured inks include white inks.

The coloured inks comprise at least one colouring agent. The colouring agent may be either dissolved or dispersed in the liquid medium of the ink. Preferably the colouring agent is a dispersible pigment, of the types known in the art and commercially available such as under the trade-names Paliotol (available from BASF plc), Cinquasia, Irgalite (both available from Ciba Speciality Chemicals) and Hostaperm (available from Clariant UK). The pigment may be of any desired colour such as, for example, Pigment Yellow 13, Pigment Yellow 83, Pigment Red 9, Pigment Red 184, Pigment Blue 15:3, Pigment Green 7, Pigment Violet 19, Pigment Black 7. Especially useful are black and the colours required for trichromatic process printing. Mixtures of pigments may be used.

In one aspect the following pigments are preferred. Cyan: phthalocyanine pigments such as Phthalocyanine blue 15.4. Yellow: azo pigments such as Pigment yellow 120, Pigment yellow 151 and Pigment yellow 155. Magenta: quinacridone pigments, such as Pigment violet 19 or mixed crystal quinacridones such as Cromophtal Jet magenta 2BC and Cinquasia RT-355D. Black: carbon black pigments such as Pigment black 7.

Pigment particles dispersed in the ink should be sufficiently small to allow the ink to pass through an inkjet nozzle, typically having a particle size less than 8 µm, preferably less than 5 µm, more preferably less than 1 µm and particularly preferably less than 0.5 µm.

The colorant is preferably present in an amount of 20 weight% or less, preferably 10 weight% or less, more preferably 8 weight% or less and most preferably 2 to 5% by weight, based on the total weight of the ink. A higher concentration of pigment may be required for white inks, however, for example up to and including 30 weight%, or 25 weight% based on the total weight of the ink.

The inks may be in the form of an ink set comprising a cyan ink, a magenta ink, a yellow ink and a black ink (a so-called trichromatic set). The inks in a trichromatic set can be used to produce a wide range of colours and tones.

The inkjet ink exhibits a desirable low viscosity (200 mPas or less, preferably 100 mPas or less, more preferably 25 mPas or less and most preferably 15 mPas or less.

In order to produce a high quality printed image a small jetted drop size is desirable. Furthermore, small droplets have a higher surface area to volume ratio when compared to larger drop sizes, which facilitates evaporation of solvent from the jetted ink. Small drop sizes therefore offer advantages in drying speed. Preferably the inkjet ink of the invention is jetted at drop sizes below 50 picolitres, preferably below 30 picolitres and most preferably below 10 picolitres.

Ink viscosity may be measured using a Brookfield viscometer fitted with a thermostatically controlled cup and spindle arrangement, such as a DV1 low-viscosity viscometer running at 20 rpm at 25 ºC with spindle 00.

Other components of types known in the art may be present in the ink to improve the properties or performance. These components may be, for example, surfactants, defoamers, dispersants, synergists for the photoinitiator, stabilisers against deterioration by heat or light, reodorants, flow or slip aids, biocides and identifying tracers.

In one aspect of the invention the surface tension of the ink is controlled by the addition of one or more surface active materials such as commercially available surfactants. Adjustment of the surface tension of the inks allows control of the surface wetting of the inks on various substrates, for example, plastic substrates. Too high a surface tension can lead to ink pooling and/or a mottled appearance in high coverage areas of the print. Too low a surface tension can lead to excessive ink bleed between different coloured inks. The surface tension is preferably in the range of 20-32 mNm^{-1} and more preferably 21-27 mNm^{-1}.

The ink may be prepared by known methods such as stirring with a high-speed water-cooled stirrer, or milling on a horizontal bead-mill.

The ink of the present invention is formulated for printing onto polyethylene terephthalate (PET) containers, and particularly PET bottles. However, it could be used on other substrates, such as PVC, polyester, PETG, polyethylene and polypropylene. Accordingly, the present invention also provides a substrate having the ink as defined herein printed thereon, and particularly where the substrate is a PET container

The printing is preferably all performed by inkjet printing, e.g. on a single-pass inkjet printer, for example for printing (directly) onto packaging, such as food packaging or bottles. Evaporation of the solvent can occur simply by exposure of the inks to the atmosphere, but the inks may also be heated to accelerate evaporation. In addition, the inks are exposed to actinic radiation to cure the ink.

Accordingly, the present invention further provides a method of inkjet printing comprising the following steps: inkjet printing the ink as defined herein onto a substrate and, in either order, evaporating the solvent and exposing the ink to actinic radiation to cure the radiation-curable oligomer and, if present, the radiation-curable monomer. Optionally, prior to evaporating the solvent/curing the ink, the ink may be partially cured (i.e. “pinning” by exposure to actinic radiation, typically UV, e.g. by LED. The substrate for the method is preferably a PET container.

It should be noted that the terms “dry” and “cure” are often used interchangeably in the art when referring to radiation-curable inkjet inks to mean the conversion of the inkjet ink from a liquid to solid by polymerisation and/or crosslinking of the radiation-curable material. Herein, however, by “drying” is meant the removal of the solvent by evaporation and by “curing” is meant the polymerisation and/or crosslinking of the radiation-curable material. Further details of the printing, drying and curing process are provided in WO 2011/021052.

The invention will now be described with reference to the following examples, which are not intended to be limiting.

Examples

Example 1

An inkjet ink was prepared according to the formulation set out in Table 1. The inkjet ink formulation was prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

Table 1.

Component	**Amount (% by weight)**
Butoxyl (solvent)	67.4
LTH (passive resin)	12.75
DPHA (hexafunctional monomer)	7.25
Cyan pigment dispersion	6
Irgacure 815 (free-radical photoinitiator)	4
Irgacure 2959 (free-radical photoinitiator)	2
Byk 331 (surfactant)	0.1
UV12 (stabiliser)	0.5
Total	100.0

Example 2

The viscosity of the ink was measured using a Brookfield viscometer fitted with a thermostatically controlled cup and spindle arrangement, such as a DV1 low-viscosity viscometer running at 20 rpm at 25ºC with spindle 00. The viscosity was measured as 8.3 mPas.

The ink was then printed onto a PET substrate, using a 12 micron K-bar onto a corona discharge-treated proprietary PET substrate and dried for 3 minutes at 60ºC then UV cured at 25 m/min using a 1 x 120 W/cm^2 medium-pressure mercury lamp.

The solvent resistance was measured using an IPA ink rub test. The double rub test is well known in the art. The ink is applied to the substrate by any suitable means. It is then dried and cured. One then takes a lint-free (cotton) cloth saturated in the solvent. One then carries out a double rub, each rub being 10 cm. The number of rubs is counted until the substrate is visible under the ink. Optionally a coloured solvent-based ink, preferably having one rub solvent resistance, may be printed under the ink to be tested so that the colour is easily visible. The substrate will then become visible when the colour is removed. The ink of Example 1 showed a very high solvent resistance of 70-80 double rubs.

Claims

1. A hybrid inkjet ink comprising: (i) at least 30% by weight of an organic solvent based on the total weight of the ink; (ii) a radiation-curable oligomer and/or a radiation-curable multifunctional monomer; (iii) a photoinitiator; (iv) optionally a colorant; and (v) 8-25% by weight, based on the total weight of the ink, of a passive thermoplastic resin having a weight-average molecular weight of 1,500 to 70,000.

2. An ink as claimed in claim 1, wherein the ink contains 60-75% by weight of an organic solvent based on the total weight of the ink.

3. An ink as claimed in claim 1 or 2, wherein the ink comprises less than 5% by weight of water based on the total weight of the ink.

4. An ink as claimed in any preceding claim, wherein the total amount of the radiation-curable oligomer and radiation-curable multifunctional monomer present in the ink is 5 to 30% by weight based on the total weight of the ink.

5. An ink as claimed in any preceding claim, wherein the ink comprises less than 5% by weight of radiation-curable monofunctional monomers based on the total weight of the ink.

6. An ink as claimed in any preceding claim, wherein the radiation-curable oligomer is present and is multifunctional.

7. An ink as claimed in any preceding claim, wherein the radiation-curable multifunctional monomer is present and is trifunctional or higher.

8. An ink as claimed in any preceding claim, wherein the colorant is present and the colorant is a dispersed pigment.

9. A method of inkjet printing comprising the following steps: inkjet printing the ink as claimed in any preceding claim onto a substrate and, in either order, evaporating the solvent and exposing the ink to actinic radiation to cure the radiation-curable oligomer and, if present, the radiation-curable monomer.

10. A method as claimed in claim 9, wherein the substrate is a PET container.

11. A substrate having the ink as claimed in any of claims 1 to 8 printed thereon.

12. A substrate as claimed in claim 11, wherein the substrate is a PET container.

AMENDED CLAIMS
received by the International Bureau on
29 September 2014 (29.09.2014)

Claims

1. A hybrid inkjet ink comprising: (i) at least 30% by weight of an organic solvent based on the total weight of the ink; (ii) a radiation-curable oligomer and/or a radiation-curable multifunctional monomer; (iii) a photoinitiator; (iv) 10% by weight or less of a colorant, based on the total weight of the ink; and (v) 8-25% by weight, based on the total weight of the ink, of a passive thermoplastic resin having a weight-average molecular weight of 1,500 to 70,000.

2. An ink as claimed in claim 1, wherein the ink contains 60-75% by weight of an organic solvent based on the total weight of the ink.

3. An ink as claimed in claim 1 or 2, wherein the ink comprises less than 5% by weight of water based on the total weight of the ink.

4. An ink as claimed in any preceding claim, wherein the total amount of the radiation-curable oligomer and radiation-curable multifunctional monomer present in the ink is 5 to 30% by weight based on the total weight of the ink.

5. An ink as claimed in any preceding claim, wherein the ink comprises less than 5% by weight of radiation-curable monofunctional monomers based on the total weight of the ink.

6. An ink as claimed in any preceding claim, wherein the radiation-curable oligomer is present and is multifunctional.

7. An ink as claimed in any preceding claim, wherein the radiation-curable multifunctional monomer is present and is trifunctional or higher.

8. An ink as claimed in any preceding claim, wherein the colorant is present and the colorant is a dispersed pigment.

9. A method of inkjet printing comprising the following steps: inkjet printing the ink as claimed in any preceding claim onto a substrate and, in either order, evaporating the solvent and exposing the ink to actinic radiation to cure the radiation-curable oligomer and, if present, the radiation-curable monomer.

10. A method as claimed in claim 9, wherein the substrate is a PET container.

11. A substrate having the ink as claimed in any of claims 1 to 8 printed thereon.

12. A substrate as claimed in claim 11, wherein the substrate is a PET container.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2014/051588

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/10 C09D11/00
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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/014933 A1 (SUN LIZHONG [US] ET AL) 18 January 2007 (2007-01-18)	1-9,11
Y	paragraph [0018]; claims 1-23; example 1	10,12

X	US 2008/030562 A1 (SUN LIZHONG [US]) 7 February 2008 (2008-02-07)	1-9,11
Y	paragraph [0026]; examples 1, 2	10,12

X	EP 1 048 700 A1 (SEIKO EPSON CORP [JP]; JSR CORP [JP]) 2 November 2000 (2000-11-02)	1-9,11
A	paragraphs [0055], [0056]; examples 1-3	10,12

X	JP 2008 007772 A (FUJIFILM CORP) 17 January 2008 (2008-01-17)	1-9,11
Y	paragraph [0241]; example 6	10,12

	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] 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	Date of mailing of the international search report
25 July 2014	01/08/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Inzenhofer, Kathrin

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2014/051588

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2 463 346 A1 (SIEGWERK BENELUX SA [BE]) 13 June 2012 (2012-06-13) paragraphs [0006] - [0009], [0012]; examples 1-6	1-12
Y	EP 1 803 784 A2 (FUJIFILM CORP [JP]) 4 July 2007 (2007-07-04) paragraph [0088]	1-12
Y	WO 2012/110802 A1 (SERICOL LTD [GB]; GOULD NIGEL [GB]; WARD JEREMY [GB]; FASSAM ROBERT [G) 23 August 2012 (2012-08-23) examples 1-3	1-12
A	WO 2008/015474 A1 (SERICOL LTD [GB]; OWEN TIMOTHY GEOFFREY [GB]; BORG KATIE LOUISE [GB]) 7 February 2008 (2008-02-07) claims 1-11; example 1	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2014/051588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007014933 A1	18-01-2007	CN 1896157 A	17-01-2007
		JP 2007051278 A	01-03-2007
		KR 20070009439 A	18-01-2007
		US 2007014933 A1	18-01-2007
US 2008030562 A1	07-02-2008	NONE	
EP 1048700 A1	02-11-2000	CN 1281151 A	24-01-2001
		DE 60031599 T2	06-09-2007
		EP 1048700 A1	02-11-2000
		JP 3940523 B2	04-07-2007
		JP 2000310706 A	07-11-2000
		TW I294974 B	21-03-2008
		US 2002128351 A1	12-09-2002
JP 2008007772 A	17-01-2008	NONE	
EP 2463346 A1	13-06-2012	CN 103534319 A	22-01-2014
		EP 2463346 A1	13-06-2012
		EP 2652053 A1	23-10-2013
		WO 2012080146 A1	21-06-2012
EP 1803784 A2	04-07-2007	AT 518923 T	15-08-2011
		EP 1803784 A2	04-07-2007
		EP 2383314 A1	02-11-2011
		US 2007146430 A1	28-06-2007
		US 2010298494 A1	25-11-2010
		US 2012149797 A1	14-06-2012
WO 2012110802 A1	23-08-2012	CN 103547458 A	29-01-2014
		EP 2675627 A1	25-12-2013
		JP 2014511288 A	15-05-2014
		US 2014063154 A1	06-03-2014
		WO 2012110802 A1	23-08-2012
WO 2008015474 A1	07-02-2008	GB 2450856 A	07-01-2009
		WO 2008015474 A1	07-02-2008