



(51) International Patent Classification:

C09D 11/101 (2014.01) C09D 11/40 (2014.01)
C09D 11/322 (2014.01)

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).

(21) International Application Number:

PCT/GB2018/050386

Published:

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

(22) International Filing Date:

13 February 2018 (13.02.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1702331.8 13 February 2017 (13.02.2017) GB
1717475.6 24 October 2017 (24.10.2017) GB
1801688.1 01 February 2018 (01.02.2018) GB

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(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, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, 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, ST, 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,

(54) Title: PRINTING METHOD AND INK

(57) Abstract: The present invention provides a method of inkjet printing comprising the steps of: (i) providing an inkjet ink comprising at least 20% by weight of isobornyl acrylate based on the total weight of the ink, 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer based on the total weight of the ink, a passive resin, a radical photoinitiator, and optionally a colorant; (ii) inkjet printing the inkjet ink onto a polypropylene or corona-treated polystyrene substrate; and (iii) curing the inkjet ink. The present invention also provides an inkjet ink comprising: at least 20% by weight of isobornyl acrylate, based on the total weight of the ink; 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink; 1-9% by weight of a difunctional (meth)acrylate monomer, based on the total weight of the ink; a passive resin; a radical photoinitiator; and optionally a colorant.



Printing method and ink

The present invention relates to a method of printing, and in particular to a method of inkjet printing onto polypropylene and corona-treated polystyrene substrates. The invention further provides a printing ink, and in particular an inkjet ink that provides a good adhesion to polypropylene and corona-treated polystyrene substrates.

In inkjet printing, minute droplets of black, white or coloured ink are ejected in a controlled manner from one or more reservoirs or printing heads through narrow nozzles onto a substrate which is moving relative to the reservoirs. The ejected ink forms an image on the substrate. The resulting image should be as high quality as possible.

For high-speed printing, the inks must flow rapidly from the printing heads, and, to ensure that this happens, they must have in use a low viscosity, typically 200 mPas or less at 25°C, although in most applications the viscosity should be 50 mPas or less, and often 25 mPas or less. Typically, when ejected through the nozzles, the ink has a viscosity of less than 25 mPas, preferably 5-15 mPas and most preferably between 7-11 mPas at the jetting temperature which is often elevated to, but not limited to 40-50°C (the ink might have a much higher viscosity at ambient temperature). The inks must also be resistant to drying or crusting in the reservoirs or nozzles. For these reasons, inkjet inks for application at or near ambient temperatures are commonly formulated to contain a large proportion of a mobile liquid vehicle or solvent such as water or a low-boiling solvent or mixture of solvents.

Another type of inkjet ink contains unsaturated organic compounds, termed monomers and/or oligomers which polymerise by irradiation, commonly with ultraviolet light, in the presence of a photoinitiator. This type of ink has the advantage that it is not necessary to evaporate the liquid phase to dry the print; instead the print is exposed to radiation to cure or harden it, a process which is more rapid than evaporation of solvent at moderate temperatures.

Inks which cure by the polymerisation of monomers may contain a wide variety of monofunctional, difunctional and multifunctional monomers. The challenge is to provide the necessary printing properties, such as good adhesion, whilst providing a high-quality image, without compromising the jetting properties. This is made all the harder in inks which are formulated without the use of water or volatile organic solvents (which also have their own disadvantages). The printing of ink images onto polypropylene and corona-treated polystyrene substrates is a significant challenge as it is difficult to gain adhesion thereto.

There is therefore a need in the art for a method of inkjet printing onto polypropylene and corona-treated polystyrene substrates, where good adhesion is achieved between the ink image and the

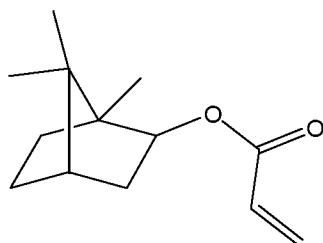
polypropylene or corona-treated polystyrene substrate. There is also a need in the art for an inkjet ink that has good adhesion to polypropylene and corona-treated polystyrene substrates.

Accordingly, the present invention provides a method of inkjet printing comprising the steps of: (i) providing an inkjet ink comprising at least 20% by weight of isobornyl acrylate based on the total weight of the ink, 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer based on the total weight of the ink, a passive resin, a radical photoinitiator, and optionally a colorant; (ii) inkjet printing the inkjet ink onto a polypropylene or corona-treated polystyrene substrate; and (iii) curing the inkjet ink.

The present invention further provides an inkjet ink comprising: at least 20% by weight of isobornyl acrylate, based on the total weight of the ink; 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink; 1-9% by weight of a difunctional (meth)acrylate monomer, based on the total weight of the ink; a passive resin; a radical photoinitiator; and optionally a colorant.

The inventors have surprisingly found that the method of inkjet printing leads to good adhesion to polypropylene or corona-treated polystyrene substrates. This is because the inkjet ink used in the method and the inkjet ink of the invention has been adapted to provide such improved adhesion.

The inkjet ink comprises at least 20% by weight of isobornyl acrylate, based on the total weight of the ink. Isobornyl acrylate (IBOA) is a well-known monomer in the art. It is a monofunctional (meth)acrylate monomer having the following chemical structure:



Isobornyl acrylate (IBOA)
mol wt 208 g/mol

It has surprisingly been found that at least 20% by weight of IBOA, based on the total weight of the ink, is necessary to achieve good adhesion to polypropylene or corona-treated polystyrene substrates.

In a preferred embodiment, the inkjet ink comprises at least 35% by weight, preferably 36-55% by weight, more preferably 36-50% by weight, of isobornyl acrylate, based on the total weight of the ink.

- 5 The inkjet ink of the invention comprises a passive resin.

Passive (or "inert") 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, a passive resin is not a radiation-curable material. The resin may be
10 selected from epoxy, polyester, vinyl, ketone, nitrocellulose, phenoxy or (meth)acrylate resins, or a mixture thereof and is preferably a poly(methyl (meth)acrylate) resin. The resin preferably has a weight-average molecular weight of 3,000 Da or above, as determined by GPC with polystyrene standards.

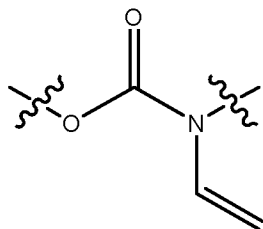
- 15 The total amount of the passive resin is preferably from 0.1-15.0% by weight, more preferably 0.2-10.0% by weight, based on the total weight of the ink.

The inventors have surprisingly found that including a passive resin in the inkjet ink helps to improve the adhesion of the inkjet ink onto a polypropylene or corona-treated polystyrene
20 substrate. The inclusion of the passive resin in the inkjet ink, in combination with the high level of IBOA, provides a crosshatch adhesion, which allows for improved adhesion onto polypropylene and corona-treated polystyrene substrates.

- 25 The inkjet ink of the invention further comprises 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink. The most preferred monomers in this class are an N-vinyl amide monomer or an N-vinyl carbamate monomer.

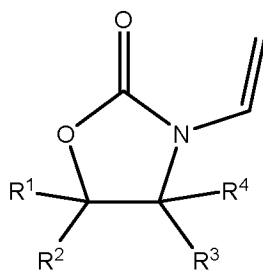
N-Vinyl amide monomers are well-known monomers in the art. N-Vinyl amide monomers have a
30 vinyl group attached to the nitrogen atom of an amide which may be further substituted in an analogous manner to the (meth)acrylate monomers as discussed below. Preferred examples are N-vinyl caprolactam (NVC) and N-vinyl pyrrolidone (NVP). Similarly, N-acryloyl amine monomers are also well-known in the art. N-acryloyl amine monomers also have a vinyl group attached to an amide but via the carbonyl carbon atom and again may be further substituted in an analogous
35 manner to the (meth)acrylate monomers. A preferred example is N-acryloylmorpholine (ACMO).

N-Vinyl carbamate monomers are defined by the following functionality:



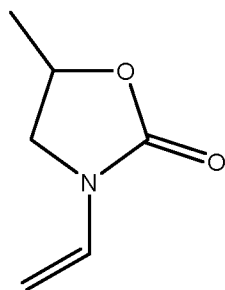
5 The synthesis of N-vinyl carbamate monomers is known in the art. For example, vinyl isocyanate, formed by the Curtius rearrangement of acryloyl azide, can be reacted with an alcohol to form N-vinyl carbamates (Phosgenations – A Handbook by L. Cotarca and H. Eckert, John Wiley & Sons, 2003, 4.3.2.8, pages 212-213).

10 In a preferred embodiment, the N-vinyl carbamate monomer is an N-vinyl oxazolidinone. N-Vinyl oxazolidinones have the following structure:



15 in which R¹ to R⁴ are not limited other than by the constraints imposed by the use in an ink-jet ink, such as viscosity, stability, toxicity etc. The substituents are typically hydrogen, alkyl, cycloalkyl, aryl and combinations thereof, any of which may be interrupted by heteroatoms. Non-limiting examples of substituents commonly used in the art include C₁₋₁₈ alkyl, C₃₋₁₈ cycloalkyl, C₆₋₁₀ aryl and combinations thereof, such as C₆₋₁₀ aryl- or C₃₋₁₈ cycloalkyl-substituted C₁₋₁₈ alkyl, any of
 20 which may be interrupted by 1-10 heteroatoms, such as oxygen or nitrogen, with nitrogen further substituted by any of the above described substituents. Preferably R¹ to R⁴ are independently selected from hydrogen or C₁₋₁₀ alkyl. Further details may be found in WO 2015/022228 and US 4,831,153.

25 Most preferably, the N-vinyl carbamate monomer is N-vinyl-5-methyl-2-oxazolidinone (NVMO). It is available from BASF and has the following structure:



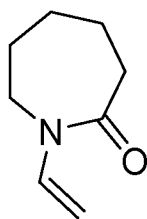
molecular weight 127 g/mol

NVMO has the IUPAC name 5-methyl-3-vinyl-1,3-oxazolidin-2-one and CAS number 3395-98-0. NVMO includes the racemate and both enantiomers. In one embodiment, the N-vinyl carbamate monomer is a racemate of NVMO. In another embodiment, the N-vinyl carbamate monomer is (R)-5-methyl-3-vinyl-1,3-oxazolidin-2-one. Alternatively, the N-vinyl carbamate monomer is (S)-5-methyl-3-vinyl-1,3-oxazolidin-2-one.

In a preferred embodiment, the inkjet ink comprises 15-25% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink.

It has surprisingly been found that such a high amount of IBOA and a passive resin as claimed in combination with 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink, allows for the inkjet ink to be printed onto a polypropylene or corona-treated polystyrene substrate, whilst achieving good adhesion to these substrates.

The most preferred N-vinyl amide monomer, N-acryloyl amine monomer and/or N-vinyl carbamate monomer is N-vinyl caprolactam (NVC) or NVMO. NVC is a well-known monomer in the art having the following chemical structure:



N-vinyl caprolactam (NVC)

mol wt 139 g/mol

In one embodiment, the N-vinyl amide monomer, N-acryloyl amine monomer and/or N-vinyl carbamate monomer present in the ink is NVC. In another embodiment, the N-vinyl amide monomer, N-acryloyl amine monomer and/or N-vinyl carbamate monomer present in the ink is NVMO.

In a preferred embodiment, the inkjet ink comprises more than 5% by weight of NVC or NVMO, based on the total weight of the ink. Preferably, the inkjet ink comprises more than 10% by weight of NVC or NVMO, based on the total weight of the ink. More preferably, the inkjet ink comprises 15-30% by weight, most preferably 15-25% by weight, of NVC or NVMO, based on the total weight of the ink.

The inkjet ink may comprise a further monofunctional (meth)acrylate monomer, other than IBOA. The further monofunctional (meth)acrylate monomer may be a cyclic monofunctional (meth)acrylate monomer and/or an acyclic-hydrocarbon monofunctional (meth)acrylate monomer. In a preferred embodiment, the further monofunctional (meth)acrylate monomer, other than IBOA, is a cyclic monofunctional (meth)acrylate monomer.

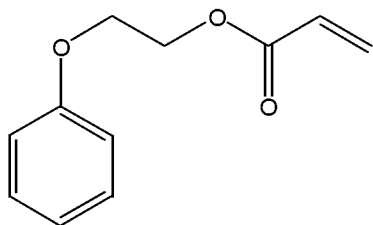
Monofunctional (meth)acrylate monomers are well known in the art and are preferably the esters of acrylic acid. A detailed description is therefore not required.

Monomers typically have a molecular weight of less than 600 Da, preferably more than 200 Da and less than 450 Da. Monomers are typically added to inkjet inks to reduce the viscosity of the inkjet ink. They therefore preferably have a viscosity of less than 150 mPas at 25°C, more preferably less than 100 mPas at 25°C and most preferably less than 20 mPas at 25°C. Monomer viscosities can be measured using an ARG2 rheometer manufactured by T.A. Instruments, which uses a 40 mm oblique / 2° steel cone at 25°C with a shear rate of 25 s⁻¹.

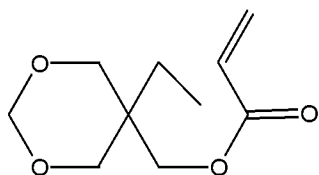
The substituents of the further monofunctional (meth)acrylate monomer, other than IBOA, are not limited other than by the constraints imposed by the use in an inkjet ink, such as viscosity, stability, toxicity etc.

The substituents of the further cyclic monofunctional (meth)acrylate monomer, other than IBOA, are typically cycloalkyl, aryl and combinations thereof, any of which may be interrupted by heteroatoms and/or substituted by alkyl. Non-limiting examples of substituents commonly used in the art include C₃₋₁₈ cycloalkyl, C₆₋₁₀ aryl and combinations thereof, any of which may be substituted with alkyl (such as C₁₋₁₈ alkyl) and/or any of which may be interrupted by 1-10 heteroatoms, such as oxygen or nitrogen, with nitrogen further substituted by any of the above-described substituents. The substituents may together also form a cyclic structure.

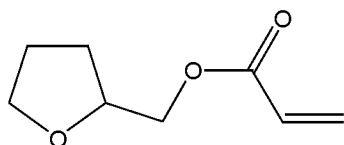
Preferably, the further cyclic monofunctional (meth)acrylate monomer, other than IBOA, is selected from phenoxyethyl acrylate (PEA), cyclic TMP formal acrylate (CTFA), tetrahydrofurfuryl acrylate (THFA), (2-methyl-2-ethyl-1,3-dioxolane-4-yl)methyl acrylate (MEDA) and mixtures thereof. PEA is particularly preferred. The preferred examples of cyclic monofunctional (meth)acrylate monomers have the following chemical structures:



Phenoxyethyl acrylate (PEA), mol wt 192 g/mol



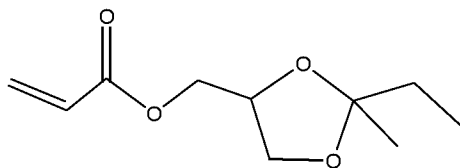
5 Cyclic TMP formal acrylate (CTFA), mol wt 200 g/mol



Tetrahydrofurfuryl acrylate (THFA)

mol wt 156 g/mol

10



(2-Methyl-2-ethyl-1,3-dioxolane-4-yl)methyl acrylate (MEDA)

mol wt 208.4 g/mol

15 Mixtures of (meth)acrylate monomers may be used.

Preferably, the inkjet ink comprises 2-50% by weight, more preferably 10-50% by weight, of a further cyclic monofunctional (meth)acrylate monomer, other than IBOA, based on the total weight of the ink.

20

Preferably, the inkjet ink comprises 20-70% by weight, more preferably 30-66% by weight, of cyclic monofunctional (meth)acrylate monomer in total, including IBOA, based on the total weight of the ink.

25 In a preferred embodiment, the inkjet ink comprises at least two cyclic monofunctional (meth)acrylate monomers, one of which is IBOA.

In a preferred embodiment, the inkjet ink comprises a second cyclic monofunctional (meth)acrylate monomer selected from cyclic TMP formal acrylate (CTFA), phenoxyethyl acrylate (PEA), tetrahydrofurfuryl acrylate (THFA), (2-methyl-2-ethyl-1,3-dioxolane-4-yl)methyl acrylate (MEDA) and mixtures thereof.

5

The most preferred is PEA. In a particularly preferred embodiment, the only cyclic monofunctional (meth)acrylate monomers present in the ink are PEA and IBOA. In a further preferred embodiment, the ink contains no other monofunctional (meth)acrylate monomers, i.e. it is substantially free of other acyclic-hydrocarbon monofunctional (meth)acrylate monomers. In a particularly preferred embodiment, the only monofunctional (meth)acrylate monomers present in the ink are PEA and IBOA.

10

The substituents of the acyclic-hydrocarbon monofunctional (meth)acrylate monomer are typically alkyl, which may be interrupted by heteroatoms. A non-limiting example of a substituent commonly used in the art is C₁₋₁₈ alkyl, which may be interrupted by 1-10 heteroatoms, such as oxygen or nitrogen, with nitrogen being further substituted.

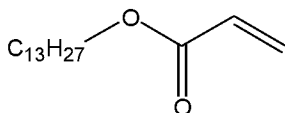
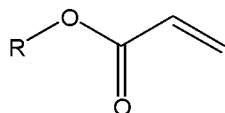
15

Preferably, the acyclic-hydrocarbon monofunctional (meth)acrylate monomer contains a linear or branched C₆-C₂₀ group. In a preferred embodiment, the acyclic-hydrocarbon monofunctional (meth)acrylate monomer is selected from octadecyl acrylate (ODA), 2-(2-ethoxyethoxy)ethyl acrylate (EOEOEA), tridecyl acrylate (TDA), isodecyl acrylate (IDA), lauryl acrylate and mixtures thereof.

20

The preferred examples of acyclic-hydrocarbon monofunctional (meth)acrylate monomers have the following chemical structures:

25



R = C₈H₁₇ / C₁₀H₂₁

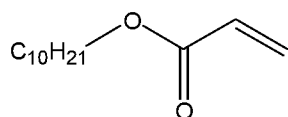
Octadecyl acrylate (ODA)

mol wt 200 g/mol

Tridecyl acrylate (TDA)

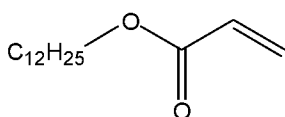
mol 254 g/mol

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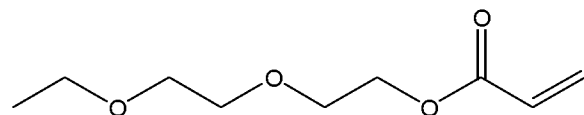
Isodecyl acrylate (IDA)

mol wt 212 g/mol



Lauryl acrylate

mol wt 240 g/mol



35

2-(2-Ethoxyethoxy)ethyl acrylate (EOEOEA), mol wt 188 g/mol

Mixtures of (meth)acrylate monomers may be used.

5 In a preferred embodiment, the inkjet ink further comprises 1-9% by weight of a difunctional (meth)acrylate monomer, based on the total weight of the ink.

Difunctional (meth)acrylate monomers are well known in the art and a detailed description is therefore not required. Difunctional has its standard meaning, i.e. two groups, which take part in the polymerisation reaction on curing.

10

The substituents of the difunctional monomers are not limited other than by the constraints imposed by the use in an inkjet ink, such as viscosity, stability, toxicity etc. The substituents are typically alkyl, cycloalkyl, aryl and combinations thereof, any of which may be interrupted by heteroatoms. Non-limiting examples of substituents commonly used in the art include C₁₋₁₈ alkyl, 15 C₃₋₁₈ cycloalkyl, C₆₋₁₀ aryl and combinations thereof, such as C₆₋₁₀ aryl- or C₃₋₁₈ cycloalkyl-substituted C₁₋₁₈ alkyl, any of which may be interrupted by 1-10 heteroatoms, such as oxygen or nitrogen, with nitrogen further substituted by any of the above-described substituents. The substituents may together also form a cyclic structure.

20 Preferred examples include hexanediol diacrylate, 1,8-octanediol diacrylate, 1,9-nonanediol diacrylate, 1,10-decanediol diacrylate, 1,11-undecanediol diacrylate and 1,12-dodecanediol diacrylate, polyethyleneglycol diacrylate (for example tetraethyleneglycol diacrylate), dipropyleneglycol diacrylate (DPGDA), tripropylene glycol diacrylate (TPGDA), neopentylglycol diacrylate, 3-methyl pentanediol diacrylate, tricyclodecane dimethanol diacrylate (TCDDMDA) 25 and the acrylate esters of ethoxylated or propoxylated glycols and polyols, for example, propoxylated neopentyl glycol diacrylate, and mixtures thereof.

In addition, suitable difunctional methacrylate monomers also include esters of methacrylic acid (i.e. methacrylates), such as hexanediol dimethacrylate, 1,8-octanediol dimethacrylate, 1,9- 30 nonanediol dimethacrylate, 1,10-decanediol dimethacrylate, tricyclodecane dimethanol diacrylate, 1,11-undecanediol dimethacrylate and 1,12-dodecanediol dimethacrylate. triethyleneglycol dimethacrylate, diethyleneglycol dimethacrylate, ethyleneglycol dimethacrylate, 1,4-butanediol dimethacrylate and mixtures thereof.

35 Although less preferred, the difunctional (meth)acrylate monomer may also be selected from polyethylene glycol (200) diacrylate, polyethylene glycol (300) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate, ethoxylated (5) hexanediol diacrylate, ethoxylated (4) bisphenol A diacrylate and ethoxylated (10) bisphenol A diacrylate.

Preferably, the inkjet ink comprises less than 10% by weight, more preferably less than 5% by weight, of a difunctional (meth)acrylate monomer, based on the total weight of the ink, although some difunctional (meth)acrylate monomer is tolerated. For example, the inkjet ink may comprise at least 1% by weight, preferably 1-9% by weight, more preferably 1-5% by weight, of difunctional (meth)acrylate monomer, based on the total weight of the ink.

When a difunctional (meth)acrylate monomer is included, the difunctional (meth)acrylate monomer is more preferably selected from 1,4-butanediol diacrylate, 3-methyl-1,5-pentanediol diacrylate, 1,6-hexanediol diacrylate, 1,8-octanediol dimethacrylate, 1,9-nonanediol diacrylate, 1,10-decanediol diacrylate, 1,11-undecanediol dimethacrylate, 1,12-dodecanediol dimethacrylate, tricyclodecane dimethanol diacrylate, tripropylene glycol diacrylate, dipropylene glycol diacrylate and tetraethylene glycol diacrylate. These difunctional monomers are particularly advantageous with respect to adhesion onto polypropylene and corona-treated polystyrene.

More preferably, the difunctional (meth)acrylate monomer is selected from TCDDMDA, DDDA and DPGDA. These monomers are particularly advantageous with respect to adhesion onto polypropylene and corona-treated polystyrene.

TCDDMDA is the most preferred difunctional monomer. TCDDMDA is particularly advantageous with respect to blocking resistance.

It has surprisingly been found that a difunctional (meth)acrylate monomer can be included in the inkjet ink of the present invention, and as such can achieve advantages associated with the inclusion of difunctional (meth)acrylate monomer, such as improved gloss and blocking, without having a detrimental effect on the other printing and jetting properties of the ink, whilst maintaining a high-quality image with good adhesion onto polypropylene and corona-treated polystyrene substrates.

However, the inventors have found that the inclusion of at least 10% by weight of difunctional (meth)acrylate monomer, based on the total weight of the ink, leads to poor adhesion onto polypropylene and corona-treated polystyrene substrates.

Mixtures of (meth)acrylate monomers may also be used.

The inkjet ink may further comprise a multifunctional (meth)acrylate monomer. Multifunctional (meth)acrylate monomers (which do not include difunctional (meth)acrylate monomers) are well known in the art and a detailed description is therefore not required. Multifunctional has its standard meaning, i.e. tri or higher, that is three or more groups, respectively, which take part in the polymerisation reaction on curing. Preferably, the multifunctional (meth)acrylate monomer has a degree of functionality of four or more, more preferably a degree of functionality of from 4-8.

The substituents of the multifunctional monomers are not limited other than by the constraints imposed by the use in an inkjet ink, such as viscosity, stability, toxicity etc. The substituents are typically alkyl, cycloalkyl, aryl and combinations thereof, any of which may be interrupted by heteroatoms. Non-limiting examples of substituents commonly used in the art include C₁₋₁₈ alkyl, C₃₋₁₈ cycloalkyl, C₆₋₁₀ aryl and combinations thereof, such as C₆₋₁₀ aryl- or C₃₋₁₈ cycloalkyl-substituted C₁₋₁₈ alkyl, any of which may be interrupted by 1-10 heteroatoms, such as oxygen or nitrogen, with nitrogen further substituted by any of the above described substituents. The substituents may together also form a cyclic structure.

Suitable multifunctional (meth)acrylate monomers include tri-, tetra-, penta-, hexa-, hepta- and octa-functional monomers. Examples of the multifunctional acrylate monomers that may be included in the inkjet inks include trimethylolpropane triacrylate, pentaerythritol triacrylate, tri(propylene glycol) triacrylate, bis(pentaerythritol) hexaacrylate, and the acrylate esters of ethoxylated or propoxylated glycols and polyols, for example, ethoxylated trimethylolpropane triacrylate, and mixtures thereof. Suitable multifunctional (meth)acrylate monomers also include esters of methacrylic acid (i.e. methacrylates), such as trimethylolpropane trimethacrylate. Mixtures of (meth)acrylate monomers may also be used.

Multifunctional (meth)acrylate monomer may be present in an amount of 1-10% by weight, preferably 2-8% by weight, based on the total weight of the ink.

In a preferred embodiment, the inkjet ink comprises low levels of multifunctional monomers (including multifunctional (meth)acrylate monomers), i.e. no more than 5% by weight, more preferably no more than 2%, based on the total weight of the ink. The ink is preferably substantially free of multifunctional monomers (including multifunctional (meth)acrylate monomers). Preferably, the ink comprises less than 2% by weight, more preferably less than 1% by weight and most preferably less than 0.5% by weight, of multifunctional monomers, based on the total weight of the ink.

For the avoidance of doubt, (meth)acrylate is intended herein to have its standard meaning, i.e. acrylate and/or methacrylate. Mono and difunctional are intended to have their standard meanings, i.e. one or two groups, respectively, which take part in the polymerisation reaction on curing. Multifunctional (which does not include difunctional) is intended to have its standard meaning, i.e. three or more groups, respectively, which take part in the polymerisation reaction on curing.

The inkjet ink of the present invention comprises a radical photoinitiator. 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, 2,4,6-trimethylbenzoyldiphenylphosphine 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). Preferred photoinitiators are selected from 1-hydroxycyclohexyl phenyl ketone, bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, and mixtures thereof.

Preferably, the photoinitiator is present in an amount of 1-20% by weight, preferably 1-15% by weight, based on the total weight of the ink.

Mixtures of free radical photoinitiators can be used and preferably, the ink comprises a plurality of free radical photoinitiators. The total number of free radical photoinitiators present is preferably from one to six, and more preferably, two or more free radical photoinitiators are present in the ink.

The inkjet ink may also contain a radiation-curable (i.e. polymerisable) oligomer.

The term "curable oligomer" has its standard meaning in the art, namely that the component is partially reacted to form a pre-polymer having a plurality of repeating monomer units, which is capable of further polymerisation. The oligomer preferably has a molecular weight of at least 450 Da and preferably at least 600 Da (whereas monomers typically have a molecular weight below these values). The molecular weight is preferably below 3,000 Da. 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. Thus, for polymeric materials, number average molecular weights can be obtained using gel permeation chromatography and polystyrene standards.

The degree of functionality of the oligomer determines the degree of crosslinking and hence the properties of the cured ink. The oligomer is preferably multifunctional meaning that it contains on average more than one reactive functional group per molecule. The average degree of functionality is preferably from 2 to 6.

Preferred oligomers for inclusion in the ink have a viscosity of 0.5 to 10 Pas at 50°C. Oligomer viscosities can be measured using an ARG2 rheometer manufactured by T.A. Instruments, which uses a 40 mm oblique / 2° steel cone at 60°C with a shear rate of 25 s⁻¹.

Radiation-curable oligomers comprise a backbone, for example a polyester, urethane, epoxy or polyether backbone, and one or more radiation-curable groups. The oligomer preferably comprises a polyester backbone. The polymerisable group can be any group that is capable of

polymerising upon exposure to radiation. Preferably the oligomers are (meth)acrylate oligomers, e.g. polyester acrylate oligomers.

5 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.

10 In one embodiment the radiation-curable oligomer polymerises by free-radical polymerisation. Preferably, the radiation-curable oligomer cures upon exposure to radiation in the presence of a photoinitiator to form a crosslinked, solid film.

The total amount of the oligomer and/or passive resin is preferably from 0.1-15% by weight, more preferably 0.2-10% by weight, based on the total weight of the ink.

15 The inkjet ink dries primarily by curing, i.e. by the polymerisation of the monomers present, as discussed hereinabove, and hence is a curable ink. The ink does not, therefore, require the presence of water or a volatile organic solvent to effect drying of the ink. The absence of water and volatile organic solvents means that the ink does not need to be dried to remove the water/solvent. However, water and volatile organic solvents have a significant viscosity-lowering
20 effect making formulation of the ink in the absence of such components significantly more challenging.

Accordingly, the inkjet ink is preferably substantially free of water and volatile organic solvents. Preferably, the inkjet ink comprises less than 5% by weight combined of water and volatile
25 organic solvent combined, preferably less than 3% by weight combined, more preferably, less than 2% by weight combined and most preferably less than 1% by weight combined, based on the total weight of the ink. Some water will typically be absorbed by the ink from the air and solvents may be present as impurities in the components of the inks, but such low levels are tolerated.

30 The inkjet ink may also comprise a 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
35 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.

40

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.

5 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 .

10

The colorant is preferably present in an amount of 0.2-20% by weight, preferably 0.5-10% by weight, based on the total weight of the ink. A higher concentration of pigment may be required for white inks, for example up to and including 30% by weight, or 25% by weight, based on the total weight of the ink

15

The amounts by weight provided herein are based on the total weight of the ink.

The inkjet ink exhibits a desirable low viscosity (200 mPas or less, preferably 100 mPas or less, more preferably 50 mPas or less at 25°C).

20

In order to produce a high quality printed image a small jetted drop size is desirable, particularly for high resolution images. Preferably the inkjet ink of the invention is jetted at drop sizes below 50 picolitres, preferably below 30 picolitres and most preferably below 20 picolitres.

25 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°C with spindle 00.

30 The surface tension of the inkjet ink may controlled by the addition of one or more surface active materials such as commercially available surfactants. Surfactants are well known in the art and a detailed description is not required. 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
35 inks. The surface tension is preferably in the range of 20-40 mNm^{-1} and more preferably 21-32 mNm^{-1} .

40 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, defoamers, dispersants, stabilisers against deterioration by heat or light, reodorants, flow or slip aids, biocides and identifying tracers.

The present invention also provides an inkjet ink set wherein at least one of the inks in the set is an inkjet ink comprising: at least 20% by weight of isobornyl acrylate, based on the total weight of the ink; 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink; 1-9% by weight of a difunctional (meth)acrylate monomer, based on the total weight of the ink; a passive resin; a radical photoinitiator; and optionally a colorant, wherein the inkjet ink comprises less than 10% by weight of a difunctional (meth)acrylate monomer, based on the total weight of the ink. Preferably, all of the inks in the set fall within the scope of the inkjet ink according to the present invention.

Usually, the inkjet ink set of the present invention is in the form of a multi-chromatic inkjet ink set, which typically comprises a cyan ink, a magenta ink, a yellow ink and a black ink (a so-called trichromatic set). This set is often termed CMYK. The inks in a trichromatic set can be used to produce a wide range of colours and tones.

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

A suitable printer is a flatbed UV printer, for example from the Onset series from Inca Digital.

The inks of the present invention may advantageously be printed onto low surface energy substrates, by which is meant substrates having a surface energy of 25-50 mN/m (25-50 dyne/cm). Examples of substrates include those composed of polycarbonate, polyethylene terephthalate (PET), PMMA, PVC, polystyrene, polyethylene and polypropylene. In a preferred embodiment, the substrate is polypropylene or corona-treated polystyrene. Suitable corona-treated polystyrenes include Litho Grade Corona Treated Styrene 0.08" and Digi-HIPS Grade Corona Treated Styrene 0.08", supplied by Primex.

The present invention also provides a printed substrate having the ink or inkjet ink set as defined herein printed thereon. Preferably, the substrate is polypropylene or corona-treated polystyrene.

The present invention also provides a method of inkjet printing comprising: (i) providing an inkjet ink comprising at least 20% by weight of isobornyl acrylate based on the total weight of the ink, 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer based on the total weight of the ink, a passive resin, a radical photoinitiator, and optionally a colorant; (ii) inkjet printing the inkjet ink onto a polypropylene or corona-treated polystyrene substrate; and (iii) curing the inkjet ink.

Printing is performed by inkjet printing, e.g. on a single-pass inkjet printer, for example for printing (directly) onto the substrate, on a roll-to-roll printer or a flat-bed printer.

The inks or inkjet ink set are exposed to actinic (often UV) radiation to cure the ink. The exposure to actinic radiation may be performed in an inert atmosphere, e.g. using a gas such as nitrogen, in order to assist curing of the ink.

5

Any of the sources of actinic radiation discussed herein may be used for the irradiation of the inkjet ink. A suitable dose would be greater than 200 mJ/cm^2 , more preferably at least 300 mJ/cm^2 and most preferably at least 500 mJ/cm^2 . The upper limit is less relevant and will be limited only by the commercial factor that more powerful radiation sources increase cost. A typical upper limit would be 5 J/cm^2 . Further details of the printing and curing process are provided in WO 2012/110815.

10

Upon exposure to a radiation source, the ink cures to form a relatively thin polymerised film. The ink of the present invention typically produces a printed film having a thickness of 1 to $20 \mu\text{m}$, preferably 1 to $10 \mu\text{m}$, for example 2 to $5 \mu\text{m}$. Film thicknesses can be measured using a confocal laser scanning microscope.

15

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

20

Examples

Example 1

Inkjet ink 1 and reference inkjet inks 1-4 were prepared according to the formulations set out in Table 1. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

25

Ink 1 and reference inks 1-4 each contain the passive resin BR113. Ink 1 and reference inks 1-4 have different monofunctional monomers as the predominant monofunctional monomer (IBOA, PEA, EOEOEA, IDA and CTFA, respectively).

30

Table 1. Ink 1 and reference inks 1-4 containing 2% BR113

	Ink 1	Ref ink 1	Ref ink 2	Ref ink 3	Ref ink 4
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	22.0	62.0	22.0	22.0	22.0
EOEOEA	-	-	40.0	-	-
IDA	-	-	-	40.0	-
CTFA	-	-	-	-	40.0
IBOA	40.0	-	-	-	-
NVC	16.5	16.5	16.5	16.5	16.5
BR113	2.0	2.0	2.0	2.0	2.0
IRG184	4.0	4.0	4.0	4.0	4.0
TPO	8.0	8.0	8.0	8.0	8.0
UV12	0.5	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6.0	6.0	6.0	6.0	6.0
BYK307	1.0	1.0	1.0	1.0	1.0
TOTAL	100.0	100.0	100.0	100.0	100.0

IRG184 and TPO are photoinitiators. UV12 is a stabiliser. BYK307 is a surfactant.

- 5 The cyan pigment dispersions of the inks of Table 1 were prepared according to the following formulation. The cyan pigment dispersion contains 59% PEA, 1% stabiliser, 10% dispersant and 30% blue pigment. The dispersions were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the dispersion.
- 10 The inks of Table 1 were drawn down onto various polypropylene and polystyrene substrates as listed in Table 3 using a no.2 K bar applicator depositing a 12 micron wet film. The prints were cured by exposure to UV radiation. The doses and intensities of the UV lamp used for curing are set out in Table 2 below. Cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and
- 15 1 is poor adhesion. The results can be seen in Table 3.

Table 2

Cure radiation					
	UVA	UVB	UVC	UVV	Total
Dose (mJ/cm ²)	330.10	324.24	60.14	256.46	970.94
Intensity (mW/cm ²)	828.80	824.96	148.56	643.32	2445.64

Table 3

Adhesion						
Test	Substrate	Ink 1	Ref ink 1	Ref ink 2	Ref ink 3	Ref ink 4
Initial crosshatch (ISO tape)	Litho Styrene 0.08"	5	5	5	5*	5
	DigiHIPS Styrene 0.08"	5	5	5	5*	5
	Litho Styrene 0.08" Corona Treated	5	2	5	4*	2
	DigiHIPS Styrene 0.08" Corona Treated	5	3	5	5*	4
	Stephen Webster Correx PP 3 mm	5	1	1	5*	1
	Laird Fluted PP 4 mm	5	1	4	5*	1

* Delamination of top layer by ISO tape.

5

PP is polypropylene.

As can be seen, the inclusion of IBOA as the predominant monofunctional monomer improves adhesion to polypropylene and corona-treated polystyrene.

10

The inks of Table 1 were tested for cure speed. The test for cure speed is as follows. The inks were drawn down onto a polyvinyl chloride substrate using a no.2 K bar applicator depositing a 12 micron wet film. The inks were then cured by passing them under a UV lamp. The doses and intensities per pass are set out in Table 4 below. After the first pass under the lamp, a small strip of Epson Premium Photo Paper is placed onto the printed ink, with the coated side of the paper facing the printed ink, and rubbed down 10 times by hand. Any ink removal or surface marking (offsetting) of the printed ink indicates an incomplete cure. The printed ink is repeatedly passed under the lamp and tested in this way until there is no ink removal or surface marking of the printed ink, indicating full cure. The resultant film should therefore be tack free. The results are shown in Table 5.

20

Table 4

Cure radiation per pass					
	UVA	UVB	UVC	UVV	Total
Dose (mJ/cm ²)	19.43	19.61	4.46	17.07	60.57
Intensity (mW/cm ²)	279.84	284.91	65.56	244.28	874.59

Table 5

Tack and cure speed					
	Ink 1	Ref ink 1	Ref ink 2	Ref ink 3	Ref ink 4
Tack level (gloss PVC)	Acceptable	Acceptable	Very tacky	Very tacky	Acceptable
Cure speed (mJ/cm ²)	121.118	242.236	>600	>600	181.677
Number of passes required to achieve full cure	2	4	>10	>10	3

- 5 As is apparent from Table 5, ink 1 requires only 2 passes to provide a tack free film. An “acceptable” tack level means that the cure speed is acceptable. It is clear therefore that the inclusion of IBOA as the predominant monofunctional monomer leads to a better performance with respect to cure speed than the reference inks which do not contain IBOA.

10 Comparative Example 2

Reference inkjet inks 5-9 were prepared according to the formulations set out in Table 6. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

15

The inks of Table 6 differ from the inks of Table 1 in that each ink of Table 6 contains the difunctional urethane acrylate oligomer CN964A85 instead of the passive resin BR113. Again, reference inks 5-9 have different monofunctional monomers as the predominant monofunctional monomer (IBOA, PEA, EOEOEA, IDA and CTFA, respectively).

20

Table 6. Reference inks 5-9 containing 10% CN964A85

	Ref ink 5	Ref ink 6	Ref ink 7	Ref ink 8	Ref ink 9
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	14.0	54.0	14.0	14.0	14.0
EOEOEA	-	-	40.0	-	-
IDA	-	-	-	40.0	-
CTFA	-	-	-	-	40.0
IBOA	40.0	-	-	-	-
NVC	16.5	16.5	16.5	16.5	16.5
CN964A85	10.0	10.0	10.0	10.0	10.0
IRG184	4.0	4.0	4.0	4.0	4.0
TPO	8.0	8.0	8.0	8.0	8.0
UV12	0.5	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6.0	6.0	6.0	6.0	6.0
BYK307	1.0	1.0	1.0	1.0	1.0
TOTAL	100.0	100.0	100.0	100.0	100.0

The inks of Table 6 were drawn down onto various polypropylene and polystyrene substrates as listed in Table 7 using a no.2 K bar applicator depositing a 12 micron wet film. The doses and intensities of the UV lamp used for curing are set out in Table 2 above. Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Table 7.

10 Table 7

Adhesion						
Test	Substrate	Ref ink 5	Ref ink 6	Ref ink 7	Ref ink 8	Ref ink 9
Initial crosshatch (ISO tape)	Litho Styrene 0.08"	5	5	5	5	1
	DigiHIPS Styrene 0.08"	5	5	5	5	1
	Litho Styrene 0.08" Corona Treated	1	1	5	1	1
	DigiHIPS Styrene 0.08" Corona Treated	1	1	5	1	1
	Stephen Webster Correx PP 3 mm	1	1	1	1	1
	Laird Fluted PP 4 mm	1	1	1	1	1

As can be seen, the inclusion of a difunctional oligomer in place of the passive resin leads to poor adhesion, particularly with respect to the polypropylene and corona-treated polystyrene substrates.

The inks of Table 6 were tested for cure speed using the method described in Example 1. The results are set out below in Table 8.

Table 8

Tack and cure speed					
	Ref ink 5	Ref ink 6	Ref ink 7	Ref ink 8	Ref ink 9
Tack level (gloss PVC)	Acceptable	Acceptable	Tacky	Very tacky	Acceptable
Cure speed (mJ/cm ²)	181.68	423.91	>600	>600	242.24
Number of passes required to achieve full cure	3	7	>10	>10	4

5

As can be seen, the inclusion of IBOA in reference ink 5 as the predominant monofunctional monomer leads to a better performance with respect to cure speed than the reference inks which do not contain IBOA.

10 Comparative Example 3

Reference inkjet inks 10-14 were prepared according to the formulations set out in Table 9. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

15

The inks of Table 9 differ from the inks of Table 1 in that each ink of Table 9 contains the polyester tetraacrylate resin EBECRYL 657 instead of the passive resin BR113. Again, reference inks 10-14 have different monofunctional monomers as the predominant monofunctional monomer (IBOA, PEA, EOEOEA, IDA and CTFA, respectively).

20

Table 9. Reference inks 10-14 containing 10% polyester tetrafunctional resin

	Ref ink 10	Ref ink 11	Ref ink 12	Ref ink 13	Ref ink 14
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	14.0	54.0	14.0	14.0	14.0
EOEOEA	-	-	40.0	-	-
IDA	-	-	-	40.0	-
CTFA	-	-	-	-	40.0
IBOA	40.0	-	-	-	-
NVC	16.5	16.5	16.5	16.5	16.5
EBECRYL 657	10.0	10.0	10.0	10.0	10.0
IRG184	4.0	4.0	4.0	4.0	4.0
TPO	8.0	8.0	8.0	8.0	8.0
UV12	0.5	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6.0	6.0	6.0	6.0	6.0
BYK307	1.0	1.0	1.0	1.0	1.0
TOTAL	100.0	100.0	100.0	100.0	100.0

The inks of Table 9 were drawn down onto various polypropylene and polystyrene substrates as listed in Table 10 using a no.2 K bar applicator depositing a 12 micron wet film. The doses and intensities of the UV lamp used for curing are set out in Table 2 above. Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Table 10.

10 Table 10

Adhesion						
Test	Substrate	Ref ink 10	Ref ink 11	Ref ink 12	Ref ink 13	Ref ink 14
Initial crosshatch (ISO tape)	Litho Styrene 0.08"	5	5	5	5	1
	DigiHIPS Styrene 0.08"	5	5	5	3	1
	Litho Styrene 0.08" Corona Treated	1	1	5	1	1
	DigiHIPS Styrene 0.08" Corona Treated	1	1	5	1	1
	Stephen Webster Correx PP 3 mm	1	1	1	1	1
	Laird Fluted PP 4 mm	1	1	2	1	1

As can be seen, the inclusion of a tetrafunctional resin in place of the passive resin leads to poor adhesion, particularly with respect to the polypropylene and corona-treated polystyrene substrates.

The inks of Table 9 were tested for cure speed using the method described in Example 1. The results are set out below in Table 11.

5 Table 11

Tack and cure speed					
	Ref ink 10	Ref ink 11	Ref ink 12	Ref ink 13	Ref ink 14
Tack level (gloss PVC)	Acceptable	Acceptable	Tacky	Tacky	Acceptable
Cure speed (mJ/cm ²)	181.68	545.03	>600	>600	423.91
Number of passes required to achieve full cure	3	9	10	10	7

As can be seen, the inclusion of IBOA in reference ink 11 as the predominant monofunctional monomer leads to a better performance with respect to cure speed than the reference inks which do not contain IBOA.

10

Example 4

Reference inkjet inks 15 and 16 and inkjet inks 1-3 were prepared according to the formulations set out in Table 12. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

15

The inks of Table 12 each contain the passive resin BR113. Reference inks 15 and 16 and inks 1-3 contain differing amounts of IBOA (0.0%, 10.0%, 40.0%, 20.0% and 30.0%, respectively). The cyan pigment dispersion has the same composition as the cyan pigment dispersion of Example 1.

20

Table 12. Reference inks 15 and 16 and inks 1-3 containing 0.0%, 10.0%, 20.0%, 30.0% and 40.0% IBOA

	Ref ink 15	Ref ink 16	Ink 2	Ink 3	Ink 1
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	62.0	52.0	42.0	32.0	22.0
IBOA	-	10.0	20.0	30.0	40.0
NVC	16.5	16.5	16.5	16.5	16.5
BR113	2.0	2.0	2.0	2.0	2.0
IRG184	4.0	4.0	4.0	4.0	4.0
TPO	8.0	8.0	8.0	8.0	8.0
UV12	0.5	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6.0	6.0	6.0	6.0	6.0
BYK307	1.0	1.0	1.0	1.0	1.0
TOTAL	100.0	100.0	100.0	100.0	100.0

The inks of Table 12 were drawn down onto various polypropylene and polystyrene substrates as listed in Table 13 using a no.2 K bar applicator depositing a 12 micron wet film. The doses and intensities of the UV lamp used for curing are set out in Table 2 above. Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Table 13.

Table 13

Adhesion						
Test	Substrate	Ref ink 15	Ref ink 16	Ink 2	Ink 3	Ink 1
Initial crosshatch (ISO tape)	Litho Styrene 0.08"	5	5	5	5	5
	DigiHIPS Styrene 0.08"	5	5	5	5	5
	DigiHIPS Styrene 0.08" Corona Treated	3	4	5	5	5
	Stephen Webster Correx PP 3 mm	1	1	5	5	5
	Laird Fluted PP 4 mm	1	3	5	5	5

As can be seen, the inclusion of less than 20.0% by weight of IBOA, based on the total weight of the ink, leads to poor adhesion, particularly with respect to the polypropylene and corona-treated polystyrene substrates.

The inks of Table 12 were tested for cure speed using the method described in Example 1. The results are set out below in Table 14.

Table 14

Tack and cure speed					
	Ref ink 15	Ref ink 16	Ink 2	Ink 3	Ink 1
Tack level (gloss PVC)	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable
Cure speed (mJ/cm ²)	242.24	121.12	121.12	121.12	121.12
Number of passes required to achieve full cure	4	2	2	2	2

As can be seen from Tables 13 and 14, the inclusion of at least 20% by weight of IBOA is necessary for both excellent adhesion onto polypropylene and corona-treated polystyrene and a high cure speed.

Example 5

Inkjet inks 1 and 4-6 were prepared according to the formulations set out in Table 15. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

The inks of Table 15 each contain the passive resin BR113 and 40% by weight of IBOA, based on the total weight of the ink. Inks 1 and 4-6 contain differing amounts of the difunctional (meth)acrylate monomer DPGDA (0.0%, 5.0%, 10.0% and 15.0%, respectively). The cyan pigment dispersion has the same composition as the cyan pigment dispersion of Example 1.

Table 15. Inks 1 and 4-6 containing 0.0%, 5.0%, 10.0% and 15.0% DPGDA

	Ink 1	Ink 4	Ink 5	Ink 6
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	22.0	17.0	12.0	8.0
IBOA	40.0	40.0	40.0	40.0
NVC	16.5	16.5	16.5	16.5
DPGDA	-	5.0	10.0	15.0
BR113	2.0	2.0	2.0	2.0
IRG184	4.0	4.0	4.0	4.0
TPO	8.0	8.0	8.0	8.0
UV12	0.5	0.5	0.5	0.5
Cyan Pigment Dispersion	6.0	6.0	6.0	6.0
BYK307	1.0	1.0	1.0	1.0
TOTAL	100.0	100.0	100.0	100.0

The inks of Table 15 were drawn down onto various polypropylene and polystyrene substrates as listed in Table 16 using a no.2 K bar applicator depositing a 12 micron wet film. The doses and intensities of the UV lamp used for curing are set out in Table 2 above. Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Table 16.

Table 16

Adhesion					
Test	Substrate	Ink 1	Ink 4	Ink 5	Ink 6
Initial crosshatch (ISO tape)	Litho Styrene 0.08"	5	5	5	5
	DigiHIPS Styrene 0.08"	5	5	5	5
	Litho Styrene 0.08" Corona Treated	5	4	1	1
	DigiHIPS Styrene 0.08" Corona Treated	5	4	1	1
	Stephen Webster Correx PP 3 mm	5	4	1	1
	Laird Fluted PP 4 mm	5	4	1	1

- As can be seen, the inclusion of 0-5% by weight of difunctional monomer, based on the total weight of the ink, leads to the best results for adhesion, particularly with respect to the polypropylene and corona-treated polystyrene substrates.

Tack results for the inks of Table 15 are set out below in Table 17.

Table 17

Tack				
	Ink 1	Ink 4	Ink 5	Ink 6
Tack level (gloss PVC)	Acceptable	Acceptable	Acceptable	Acceptable

As can be seen, all of the inks exhibit satisfactory tack results.

Example 6

Inkjet inks 7-10 were prepared according to the formulations set out in Table 18. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

The inks of Table 18 each contain the passive resin BR113 and approximately 40% by weight of IBOA, based on the total weight of the ink. Inks 7-10 contain different pigment dispersions (cyan, magenta, yellow and black, respectively).

Table 18. CYMK inks of the invention

	Ink 7	Ink 8	Ink 9	Ink 10
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	19.18	9.80	15.21	15.58
IBOA	40.00	39.23	40.00	40.00
NVC	16.50	20.00	20.40	17.86
BR113	2.40	1.20	2.00	1.40
IRG184	1.88	1.88	3.08	2.99
IRG379	-	-	-	1.94
TPO	8.01	8.01	8.01	7.77
ITX	0.80	0.80	0.80	1.55
BP	2.88	2.88	-	2.72
EDB	0.85	1.70	-	1.55
UV12	0.50	0.50	0.50	0.50
Hyperdispersant	-	-	1.00	-
Cyan pigment dispersion	6.00	-	-	-
Magenta pigment dispersion	-	13.00	-	-
Yellow pigment dispersion	-	-	8.00	-
Black pigment dispersion	-	-	-	5.14
BYK307	1.00	1.00	1.00	1.00
TOTAL	100.00	100.00	100.00	100.00

The cyan, magenta, yellow and black pigment dispersions of the inks of Table 18 were prepared according to the following formulations. The cyan pigment dispersion comprises 59% PEA, 1% stabiliser, 10% dispersant and 30% blue pigment. The magenta pigment dispersion comprises 56.5% PEA, 1.5% stabiliser, 12% dispersant and 30% magenta pigment. The yellow pigment dispersion comprises 58% PEA, 1% stabiliser, 7% dispersant and 34% yellow pigment. The black pigment dispersion comprises 46.5% PEA, 1.5% stabiliser, 12% dispersant and 40% black pigment. The dispersions were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the dispersion.

The inks of Table 18 were printed and cured using an Inca Onset X3 inkjet printer onto various polypropylene and polystyrene substrates in 3 pass Satin mode (130% relative ink density). Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Table 19.

Table 19

Adhesion						
Test	Print mode	Substrate	Ink 7	Ink 8	Ink 9	Ink 10
Initial crosshatch (ISO tape)	3-pass Satin mode	FSIS Correx PP 3mm	5	5	5	5
		FNAC Fluted PP 4mm	5	5	5	5
		FNAC Fluted PP 6mm	5	5	5	5
		Screen Styrene 0.08" Corona Treated	5	5	5	5
		Litho Styrene 0.08" Corona Treated	5	5	5	5
		DigiHIPS Styrene 0.08" Corona treated	5	4	5	5
		Screen Styrene 0.08"	5	5	5	5
		Litho Styrene 0.08"	5	5	5	5
		DigiHIPS Styrene 0.08"	5	5	5	5

As can be seen, the ink set of the invention exhibits excellent adhesion to various polypropylene and polystyrene substrates.

5

Example 7

Inkjet inks 11-14 were prepared according to the formulations set out in Table 20. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

10

The inks of Table 20 each contain the passive resin BR113 and approximately 40% by weight of IBOA, based on the total weight of the ink. Inks 11-14 contain different pigment dispersions (cyan, magenta, yellow and black, respectively). The cyan, magenta, yellow and black pigment dispersions have the same composition as the pigment dispersions of Example 6.

15

Table 20. CYMK inks of the invention.

	Ink 11	Ink 12	Ink 13	Ink 14
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	14.82	5.44	10.21	16.68
IBOA	40.00	39.23	40.00	40.00
NVC	16.50	20.00	20.40	17.86
TCDDMDA	5.00	5.00	5.00	5.00
BR113	2.56	1.36	2.00	2.93
IRG184	1.88	1.88	3.08	3.08
TPO	8.01	8.01	8.01	8.01
ITX	-	-	0.80	0.80
BP	2.88	2.88	-	-
EDB	0.85	1.70	-	-
UV12	0.50	0.50	0.50	0.50
Dispersant	-	-	1.00	-
Cyan pigment dispersion	6.00	-	-	-
Magenta pigment dispersion	-	13.00	-	-
Yellow pigment dispersion	-	-	8.00	-
Black pigment dispersion	-	-	-	4.14
BYK307	1.00	1.00	1.00	1.00
TOTAL	100.00	100.00	100.00	100.00

Example 8

- 5 Inkjet inks 15-18 were prepared according to the formulations set out in Table 21. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

- 10 The inks of Table 21 each contain the passive resin BR113 and approximately 40% by weight of IBOA, based on the total weight of the ink. Inks 15-18 contain different pigment dispersions (cyan, magenta, yellow and black, respectively). The cyan, magenta, yellow and black pigment dispersions have the same composition as the pigment dispersions of Example 6.

Table 21. CYMK inks of the invention.

	Ink 15	Ink 16	Ink 17	Ink 18
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	14.18	4.80	10.21	10.58
IBOA	40.00	39.23	40.00	40.00
NVC	16.50	20.00	20.40	17.86
TCDDMDA	5.00	5.00	5.00	5.00
BR113	2.40	1.20	2.00	1.40
IRG184	1.88	1.88	3.08	2.99
IRG379	-	-	-	1.94
TPO	8.01	8.01	8.01	7.77
ITX	0.80	0.80	0.80	1.55
BP	2.88	2.88	-	2.72
EDB	0.85	1.70	-	1.55
UV12	0.50	0.50	0.50	0.50
Hyperdispersant	-	-	1.00	-
Cyan pigment dispersion	6.00	-	-	-
Magenta pigment dispersion	-	13.00	-	-
Yellow pigment dispersion	-	-	8.00	-
Black pigment dispersion	-	-	-	5.14
BYK307	1.00	1.00	1.00	1.00
TOTAL	100.00	100.00	100.00	100.00

5 The inks of Table 21 were printed and cured using an Inca Onset X3 inkjet printer onto various polypropylene and polystyrene substrates in 3 pass Satin mode (130% relative ink density). Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Table 22.

Table 22

Adhesion						
Test	Print mode	Substrate	Ink 15	Ink 16	Ink 17	Ink 18
Initial crosshatch (ISO tape)	3-pass Satin mode	Stephen Webster Correx PP 3mm	4	5	5	5
		Laird Fluted PP 4mm	5	5	5	5
		Laird Fluted PP 6mm	5	5	5	4
		Screen Styrene 0.08" Corona Treated	5	5	5	5
		Litho Styrene 0.08" Corona Treated	5	5	5	5
		DigiHIPS Styrene 0.08" Corona treated	5	5	5	5
		Screen Styrene 0.08"	5	5	5	5
		Litho Styrene 0.08"	5	5	5	5
		DigiHIPS Styrene 0.08"	5	5	5	5

As can be seen, the ink set of the invention exhibits excellent adhesion to various polypropylene and polystyrene substrates.

5

Example 9

Reference inkjet inks 17-20 and inkjet inks 19-22 were prepared according to the formulations set out in Tables 23 and 24. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

The inks of Tables 23 and 24 each contain the passive resin BR113 and approximately 40% by weight of IBOA, based on the total weight of the ink. The cyan pigment dispersion of Tables 23 and 24 has the same composition as the cyan pigment dispersion of Example 6. Reference inks 17-20 and inks 19-22 contain differing amounts of NVC (0.0%, 5.0%, 10.0%, 35.0%, 15.0%, 20.0%, 25.0% and 30.0%, respectively).

Table 23. Reference inks 17-19 and ink 19 containing 0.0%, 5.0%, 10.0% and 15.0% NVC

	Ref ink 17	Ref ink 18	Ref ink 19	Ink 19
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	38.5	33.5	28.5	23.5
IBOA	40.0	40.0	40.0	40.0
NVC	0	5.0	10.0	15.0
BR113	2.0	2.0	2.0	2.0
IRG184	4.0	4.0	4.0	4.0
TPO	8.0	8.0	8.0	8.0
UV12	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6.0	6.0	6.0	6.0
BYK307	1.0	1.0	1.0	1.0
TOTAL	100	100	100	100

Table 24. Inks 20-22 and reference ink 20 containing 20.0%, 25.0%, 30.0% and 35.0% NVC

	Ink 20	Ink 21	Ink 22	Ref ink 20
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	18.5	13.5	8.5	8.5
IBOA	40	40	40	35
NVC	20	25	30	35
BR113	2.0	2.0	2.0	2.0
IRG184	4.0	4.0	4.0	4.0
TPO	8.0	8.0	8.0	8.0
UV12	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6.0	6.0	6.0	6.0
BYK307	1.0	1.0	1.0	1.0
TOTAL	100	100	100	100

- 5 The inks of Tables 23 and 24 were printed and cured using an Inca Onset X3 inkjet printer onto various polypropylene and polystyrene substrates in 3 pass Satin mode (130% relative ink density). Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Tables 25 and 26.

Table 25

Adhesion						
Test	Print mode	Substrate	Ref ink 17	Ref ink 18	Ref ink 19	Ink 19
Initial crosshatch (ISO tape)	3-pass Satin mode	Litho Styrene 0.08"	5	5	5	5
		DigiHIPS Styrene 0.08"	5	5	5	5
		Litho Styrene 0.08" Corona Treated	5	5	5	5
		DigiHIPS Styrene 0.08" Corona Treated	5	5	5	5
		Stephen Webster Correx PP 3mm	5	5	5	5
		Laird Fluted PP 4mm	5	5	5	5

Table 26

Adhesion						
Test	Print mode	Substrate	Ink 20	Ink 21	Ink 22	Ref ink 20
Initial crosshatch (ISO tape)	3-pass Satin mode	Litho Styrene 0.08"	5	5	5	5
		DigiHIPS Styrene 0.08"	5	5	5	5
		Litho Styrene 0.08" Corona Treated	5	5	4	4
		DigiHIPS Styrene 0.08" Corona Treated	5	5	5	5
		Stephen Webster Correx PP 3mm	5	5	5	5
		Laird Fluted PP 4mm	5	5	5	5

5

The inks of Tables 23 and 24 were tested for cure speed using the method described in Example 1. The results are set out below in Tables 27 and 28.

Table 27

Cure speed				
	Ref ink 17	Ref ink 18	Ref ink 19	Ink 19
Cure speed (mJ/cm ²)	303.00	182.00	182.00	121.00
Number of passes required to achieve full cure	5	3	3	2

Table 28

Cure speed				
	Ink 20	Ink 21	Ink 22	Ref ink 20
Cure speed (mJ/cm ²)	121.00	121.00	121.00	121.00
Number of passes required to achieve full cure	2	2	2	2

5

As can be seen, the inclusion of 15-25% by weight of NVC, based on the total weight of the ink, leads to the best results for both adhesion and cure speed.

Example 10

10

Reference inkjet inks 21-24 and inkjet inks 23-26 were prepared according to the formulations set out in Tables 29 and 30. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

15

The inks of Tables 29 and 30 each contain the passive resin BR113, 40% by weight of IBOA and 5% by weight of DPGDA, based on the total weight of the ink. The cyan pigment dispersion of Tables 23 and 24 has the same composition as the cyan pigment dispersion of Example 6. Reference inks 17-20 and inks 19-22 contain differing amounts of NVC (0.0%, 5.0%, 10.0%, 35.0%, 15.0%, 20.0%, 25.0% and 30.0%, respectively).

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Table 29. Reference inks 21-23 and ink 23 containing 0.0%, 5.0%, 10.0% and 15.0% NVC

	Ref ink 21	Ref ink 22	Ref ink 23	Ink 23
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	33.5	28.5	23.5	18.5
IBOA	40	40	40	40
NVC	0	5	10	15
DPGDA	5	5	5	5
BR113	2	2	2	2
IRG184	4	4	4	4
TPO	8	8	8	8
UV12	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6	6	6	6
BYK307	1	1	1	1
TOTAL	100	100	100	100

Table 30. Inks 24-26 and reference ink 24 containing 20.0%, 25.0%, 30.0% and 35.0% NVC

	Ink 24	Ink 25	Ink 26	Ref ink 24
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	13.5	8.5	8	8
IBOA	40	40	35.5	30.5
NVC	20	25	30	35
DPGDA	5	5	5	5
BR113	2	2	2	2
IRG184	4	4	4	4
TPO	8	8	8	8
UV12	0.5	0.5	0.5	0.5
Cyan pigment dispersion	6	6	6	6
BYK307	1	1	1	1
TOTAL	100	100	100	100

5

The inks of Tables 29 and 30 were printed and cured using an Inca Onset X3 inkjet printer onto various polypropylene and polystyrene substrates in 3 pass Satin mode (130% relative ink density). Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Tables 31 and 32.

10

Table 31

Adhesion						
Test	Print mode	Substrate	Ref ink 21	Ref ink 22	Ref ink 23	Ink 23
Initial crosshatch (ISO tape)	3-pass Satin mode	Litho Styrene 0.08"	5	5	5	5
		DigiHIPS Styrene 0.08"	5	5	5	5
		Litho Styrene 0.08" Corona Treated	1	2	2	4
		DigiHIPS Styrene 0.08" Corona Treated	1	2	4	5
		Stephen Webster Correx PP 3mm	1	1	1	4
		Laird Fluted PP 4mm	2	2	5	5

Table 32

Adhesion						
Test	Print mode	Substrate	Ink 24	Ink 25	Ink 26	Ref ink 24
Initial crosshatch (ISO tape)	3-pass Satin mode	Litho Styrene 0.08"	5	5	5	5
		DigiHIPS Styrene 0.08"	5	5	5	5
		Litho Styrene 0.08" Corona Treated	5	4	1	1
		DigiHIPS Styrene 0.08" Corona Treated	5	4	1	1
		Stephen Webster Correx PP 3mm	5	5	1	1
		Laird Fluted PP 4mm	5	5	5	5

5

As can be seen, the inclusion of 15-25% by weight of NVC, based on the total weight of the ink, leads to the best results for adhesion, particularly with respect to the polypropylene and corona-treated polystyrene substrates.

- 10 The inks of Tables 29 and 30 were tested for cure speed using the method described in Example 1. The results are set out below in Tables 33 and 34.

Table 33

Cure speed				
	Ref ink 21	Ref ink 22	Ref ink 23	Ink 23
Cure speed (mJ/cm ²)	242.00	242.00	182.00	182.00
Number of passes required to achieve full cure	4	4	3	3

Table 34

Cure speed				
	Ink 24	Ink 25	Ink 26	Ref ink 24
Cure speed (mJ/cm ²)	121.00	121.00	121.00	121.00
Number of passes required to achieve full cure	2	2	2	2

- 5 As can be seen, the inclusion of 15-25% by weight of NVC, based on the total weight of the ink, leads to the best results for both adhesion and cure speed.

Example 11

- 10 Inkjet inks 27-29 were prepared according to the formulations set out in Table 35. The inkjet ink formulations were prepared by mixing the components in the given amounts. Amounts are given as weight percentages based on the total weight of the ink.

- 15 The inks of Table 35 each contain the passive resin BR113, 40% by weight of IBOA, 5% by weight of the difunctional monomer DPGDA and 20% by weight of an N-vinyl amide monomer, N-acryloyl amine monomer and/or an N-vinyl carbamate monomer selected from NVC, ACOMO and NVMO, based on the total weight of the ink. The cyan pigment dispersion was the same as the cyan pigment dispersion of Example 1.

Table 35. Inks 27-29 of the invention

	Ink 27	Ink 28	Ink 29
Raw material name	Amount (wt%)	Amount (wt%)	Amount (wt%)
PEA	13.5	13.5	13.5
IBOA	40.0	40.0	40.0
NVC	20.0	-	-
ACMO	-	20.0	-
NVMO	-	-	20.0
DPGDA	5.0	5.0	5.0
BR113	2.0	2.0	2.0
IRG184	4.0	4.0	4.0
TPO	8.0	8.0	8.0
UV12	0.5	0.5	0.5
Cyan pigment dispersion	6.0	6.0	6.0
BYK307	1.0	1.0	1.0
TOTAL	100.00	100.00	100.0

The inks of Table 35 were printed and cured using an Inca Onset X3 inkjet printer onto various polypropylene and corona-treated polystyrene substrates in 3-pass Satin mode (130% relative ink density). Again, cross hatch tape adhesion was tested according to ISO2409. A score of 5 in cross hatch tape adhesion shows excellent adhesion, 3 indicates borderline adhesion and 1 is poor adhesion. The results can be seen in Table 36.

Table 36.

Adhesion					
Test	Print mode	Substrate	Ink 27	Ink 28	Ink 29
Initial crosshatch (ISO tape)	3-pass Satin mode	Litho Styrene 0.08" Corona Treated	5	4	N/A
		DigiHIPS Styrene 0.08" Corona Treated	5	4	N/A
		Stephen Webster Correx PP 3mm	5	5	N/A
		Laird Fluted PP 4mm	5	4	5

As can be seen, the inks exhibit excellent adhesion onto various polypropylene and corona-treated polystyrene substrates.

Claims

1. A method of inkjet printing comprising the steps of:

(i) providing an inkjet ink comprising at least 20% by weight of isobornyl acrylate based on the total weight of the ink, 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer based on the total weight of the ink, a passive resin, a radical photoinitiator, and optionally a colorant;

(ii) inkjet printing the inkjet ink onto a polypropylene or corona-treated polystyrene substrate; and

(iii) curing the inkjet ink.

2. A method of inkjet printing as claimed in claim 1, wherein the inkjet ink comprises 1-9% by weight of a difunctional (meth)acrylate monomer, based on the total weight of the ink.

3. An inkjet ink comprising: at least 20% by weight of isobornyl acrylate, based on the total weight of the ink; 15-30% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink; 1-9% by weight of a difunctional (meth)acrylate monomer, based on the total weight of the ink; a passive resin; a radical photoinitiator; and optionally a colorant.

4. A method of inkjet printing as claimed in claims 1 or 2 or an inkjet ink as claimed in claim 3, wherein the passive resin is selected from an epoxy resin, a polyester resin, a vinyl resin, a ketone resin, a nitrocellulose resin, a phenoxy resin, a (meth)acrylate resin and combinations thereof.

5. A method of inkjet printing as claimed in claim 4 or an inkjet ink as claimed in claim 4, wherein the passive resin is a poly(methyl (meth)acrylate) resin.

6. A method of inkjet printing as claimed in any of claims 1, 2, 4 or 5 or an inkjet ink as claimed in any of claims 3-5, wherein the passive resin has a weight-average molecular weight of 3,000 Da or above.

7. A method of inkjet printing as claimed in any of claims 1, 2 or 4-6 or an inkjet ink as claimed in any of claims 3-6, wherein the ink comprises 0.1-15.0% by weight of passive resin, based on the total weight of the ink.

8. A method of inkjet printing as claimed in any of claims 1, 2 or 4-7 or an inkjet ink as claimed in any of claims 3-7, wherein the difunctional (meth)acrylate monomer is selected from 1,4-butanediol diacrylate, 3-methyl-1,5-pentanediol diacrylate, 1,6-hexanediol diacrylate, 1,8-octanediol dimethacrylate, 1,9-nonanediol diacrylate, 1,10-decanediol diacrylate, 1,11-undecanediol dimethacrylate, 1,12-dodecanediol dimethacrylate, tricyclodecane dimethanol

diacrylate, tripropylene glycol diacrylate, dipropylene glycol diacrylate and tetraethylene glycol diacrylate, preferably 1,10-decanediol diacrylate, tricyclodecane dimethanol diacrylate and dipropylene glycol diacrylate, most preferably tricyclodecane dimethanol diacrylate (TCDDMDA).

- 5 9. A method of inkjet printing as claimed in any of claims 1, 2 or 4-8 or an inkjet ink as claimed in any of claims 3-8, wherein the ink comprises 15-25% by weight of an N-vinyl amide monomer, an N-acryloyl amine monomer and/or an N-vinyl carbamate monomer, based on the total weight of the ink.
- 10 10. A method of inkjet printing as claimed in any of claims 1, 2 or 4-9 or an inkjet ink as claimed in any of claims 3-9, wherein the N-vinyl amide monomer, the N-acryloyl amine monomer and/or the N-vinyl carbamate monomer is N-vinyl caprolactam (NVC) or N-vinyl-5-methyl-2-oxazolidinone (NVMO).
- 15 11. A method of inkjet printing as claimed in any of claims 1, 2 or 4-10 or an inkjet ink as claimed in any of claims 3-10, wherein the colorant is a dispersed pigment.
- 20 12. A method of inkjet printing as claimed in any of claims 1, 2 or 4-11 or an inkjet ink as claimed in any of claims 3-11, wherein the ink is substantially free of water and volatile organic solvents.
13. An inkjet ink set wherein at least one of the inks in the set, preferably all of the inks in the set, is an inkjet ink as claimed in any of claims 3-12.
- 25 14. A printed substrate having the ink as claimed in any of claims 3-12 or the inkjet ink set as claimed in claim 13, printed thereon.
15. A printed substrate according to claim 14, wherein the substrate is polypropylene or corona-treated polystyrene.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2018/050386

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D11/101 C09D11/322 C09D11/40
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	EP 2 228 416 A1 (TOYO INK MFG CO [JP]) 15 September 2010 (2010-09-15) examples	1-15
X	JP 2013 079383 A (TOYO INK SC HOLDINGS CO LTD) 2 May 2013 (2013-05-02) examples	1-15
X	WO 2015/022228 A1 (BASF SE [DE]) 19 February 2015 (2015-02-19) cited in the application examples	1-15
X	EP 2 653 511 A1 (FUJIFILM CORP [JP]) 23 October 2013 (2013-10-23) paragraph [0287]; examples	1-15
	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

23 March 2018

Date of mailing of the international search report

04/04/2018

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2018/050386

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 546 313 A1 (FUJIFILM CORP [JP]) 16 January 2013 (2013-01-16) paragraph [0161]; examples -----	1-15
X	EP 2 949 710 A1 (FUJIFILM CORP [JP]) 2 December 2015 (2015-12-02) paragraph [0188]; examples -----	1-15
X	EP 2 722 373 A1 (DAINIPPON INK & CHEMICALS [JP]) 23 April 2014 (2014-04-23) example 1 -----	1-15
X	EP 2 692 805 A1 (FUJIFILM CORP [JP]) 5 February 2014 (2014-02-05)	3-14
A	examples -----	1,2,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2018/050386

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 2228416	A1	15-09-2010	CN	101831214 A	15-09-2010
			EP	2228416 A1	15-09-2010
			JP	5171794 B2	27-03-2013
			JP	2010235914 A	21-10-2010
			US	2010233448 A1	16-09-2010

JP 2013079383	A	02-05-2013	JP	5729369 B2	03-06-2015
			JP	2013079383 A	02-05-2013

WO 2015022228	A1	19-02-2015	CN	105431497 A	23-03-2016
			EP	3033399 A1	22-06-2016
			ES	2655486 T3	20-02-2018
			JP	2016529360 A	23-09-2016
			US	2016193852 A1	07-07-2016
			WO	2015022228 A1	19-02-2015

EP 2653511	A1	23-10-2013	CN	103374259 A	30-10-2013
			EP	2653511 A1	23-10-2013
			JP	5606567 B2	15-10-2014
			JP	2013237834 A	28-11-2013
			US	2013295342 A1	07-11-2013

EP 2546313	A1	16-01-2013	CN	102876111 A	16-01-2013
			EP	2546313 A1	16-01-2013
			JP	5419934 B2	19-02-2014
			JP	2013018882 A	31-01-2013
			US	2013016166 A1	17-01-2013

EP 2949710	A1	02-12-2015	EP	2949710 A1	02-12-2015
			JP	6066960 B2	25-01-2017
			JP	2015224340 A	14-12-2015
			US	2015344709 A1	03-12-2015

EP 2722373	A1	23-04-2014	CA	2835076 A1	20-12-2012
			CN	103339208 A	02-10-2013
			EP	2722373 A1	23-04-2014
			JP	5252135 B1	31-07-2013
			JP	WO2012172974 A1	23-02-2015
			KR	20130108634 A	04-10-2013
			US	2014160215 A1	12-06-2014
			WO	2012172974 A1	20-12-2012

EP 2692805	A1	05-02-2014	CN	103459522 A	18-12-2013
			EP	2692805 A1	05-02-2014
			JP	2012201874 A	22-10-2012
			US	2014022299 A1	23-01-2014
			WO	2012133335 A1	04-10-2012
