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(54) **Title:** INK COMPOSITIONS

(57) **Abstract:** Provided is an ink composition, in particular an inkjet ink composition for use in inkjet printing such as drop on demand inkjet printing or continuous inkjet printing, which is suitable for radiation curing. The ink composition has an amine functional vinyl ether compound having at least two vinyl ether groups, and a monomer such as an acrylate compound. The ink composition has a viscosity of 5.0 to 70 mPa.s. The ink compositions have good in-printer properties or good print-properties.

INK COMPOSITIONS

Related Application

The present case claims priority to, and the benefit of, GB 2001675.4 filed on 07 February 2020 (07/02/2020), the contents of which are hereby incorporated by reference in their entirety.

Field of the Invention

The present invention relates to an ink composition, in particular an ink composition for radiation curing, for example, UV curing.

Background of the Invention

In ink compositions a number of factors must be balanced in order to avoid or reduce the problems associated with ink compositions.

For ink compositions that will undergo radiation curing, it is known to provide components in the ink composition having amine functionality in order to reduce the problem of oxygen inhibition of the curing process (see WO2008/074759).

The use of small molecule amine additives to provide the amine functionality can result in poor physical properties of the cured ink.

In some cases the amine functionality may be provided as part of an acrylate functional monomer (see, for example, US3845056 or EP1147098) or as large trialkylamines.

WO2008/074759 explains that improved physical properties of the cured ink may be obtained if the amine is provided as part of a polymer component. However, the use of polymeric amines increases viscosity in the ink compositions.

The viscosity of an ink composition, such as an inkjet ink composition, is important. In drop on demand inkjet printing, for example by the piezo method, the rate at which ink may be expelled from the nozzles decreases as a function of viscosity. Therefore it is important that the viscosity of the ink is low in order to achieve defect free printing at the maximum possible speed. Viscosity is also an important parameter for continuous inkjet printing as it affects the breakup of the jet after ejection.

In both cases it is desirable to maintain a low viscosity to achieve optimal print performance, such as to allow for high speed and high resolution inkjet printing.

To reduce the viscosity of radiation curable ink compositions, it is known to add small molecule vinyl ethers such as diethyleneglycol divinyl ether (DVE-2). For example, EP1358283 explains that vinyl ethers may be used as a minor component of the formulation to decrease the viscosity of the ink for efficient printing.

A further consideration for inkjet inks relates to the nozzle plate of the printer itself. Specifically, for good print quality the ink should not puddle on the nozzle plate as such puddles result in poor print quality. Nozzle plates are therefore typically coated with a low surface energy material which is resistant to wetting by the ink. This is aimed at preventing the ink spreading from the meniscus formed at the nozzle onto the nozzle plate in a way that would cause puddling on the nozzle plate.

It is desirable that inks, for example, inks for use in radiation curing have low viscosities and good in-printer performance such as good tolerance for the non-wetting coating of the nozzle plate (e.g. the ink does not significantly attack the low energy coating and hence does not result in increased wetting or puddling on the nozzle plate) in combination with good curing properties, such as reduced oxygen inhibition and good physical properties of the cured print.

It is an object of the present invention to provide ink compositions that have some of the above desirable characteristics. In particular, it is an object of the invention to provide ink composition which have a combination of good in-printer performance and good curing properties.

It is an alternative and/or additional object of the present invention to overcome or address the problems of prior art ink compositions by using the compositions of the invention or to at least provide a commercially useful alternative thereto.

Summary of the Invention

The present invention seeks to provide an ink composition, in particular an inkjet ink composition for use in inkjet printing such as drop on demand inkjet printing or continuous inkjet printing, which is suitable for radiation curing and has good in-printer properties or good print-properties.

Accordingly, in one aspect the present invention provides an ink composition comprising an amine functional vinyl ether compound having at least two vinyl ether groups, and a monomer such as an acrylate compound. Preferably, the ink composition has a viscosity of 5.0 to 70 mPa.s at 25 °C.

The ink composition is suitable for radiation curing.

In another aspect the present invention provides a printed deposit formed from the ink composition of the invention. The printed deposit comprises a cross linked polymer formed from the amine functional vinyl ether compound having at least two vinyl ether groups and the curable monomer for example the acrylate compound.

The present inventors have discovered that small molecule vinyl ethers that are typically used in inks to reduce viscosity, such as diethyleneglycol divinyl ether (DVE-2), attack the nozzle plate coating and cause a gradual loss of non-wetting properties. Thus the use of typical small molecule vinyl ether to reduce ink viscosity can result in poor print quality and poor printer compatibility.

The ink compositions of the present invention address or reduce the detrimental effect of small molecule vinyl ethers on the non-wetting properties of the nozzle plate.

The present invention is directed at inks having multiple vinyl ether functionalities together with an amine functionality in a single compound. In this way, the present invention provides an ink composition with improved physical properties of the cured ink (e.g. good cure, improved toughness or adhesion) and with good in printer properties (e.g. reduced effect on nozzle plate non-wetting or viscosity suitable for printing).

The ink composition is compatible with the components of a printer, for example an inkjet printer, and more particularly a drop on demand inkjet printer. The ink composition is suitable for application directly onto products and/or product packaging to achieve high quality images.

Preferably the ink composition described herein has a viscosity of about 5.0 to 70 mPa.s, more preferably from 10 to 35 mPa.s at 25ºC. Preferably the ink composition described herein has a viscosity of less than 70 mPa.s, preferably less than 50 mPa.s, preferably less than 35 mPa.s, and more preferably less than 25 mPa.s at 25ºC. Preferably the ink composition described herein has a viscosity of greater than 5.0 mPa.s, more preferably greater than 8 mPa.s, even more preferably greater than 10 mPa.s at 25 ºC. The viscosity of the composition may be measured using rheometer such as the MCR302 from Anton Paar or using a viscometer such as a Brookfield DV- II+ viscometer.

Preferably the ink composition as described herein has a surface tension of from 20 to 50 mN/m, more preferably from 25 to 40 mN/m at 25°C, measured by the maximum bubble pressure method at a surface age of 100ms. The surface tension of the composition may be measured using equipment such as a du Nouy ring tensiometer or using the pendant drop method on a KSV Cam 200 optical tensiometer.

Summary of Figures

Figure 1 shows photos of the nozzle plate wetting tests. Figure 1a show (from left to right) the tests using comparative nozzle plate inks 2, 3 and 4. Figure 1b shows (from left to right) the tests using nozzle plate inks 1, 2, 3, 4, 5, 6 and 7.

Detailed Description

The present invention seeks to provide an ink composition, in particular an inkjet ink composition for use in drop on demand inkjet printing, which is suitable for radiation curing and has good in-printer properties or good print-properties.

Accordingly, in one aspect the present invention provides an ink composition comprising an amine functional vinyl ether compound having at least two vinyl ether groups and a monomer such as an acrylate monomer. Preferably, the ink composition has a viscosity of 5.0 to 70 mPa.s at 25 °C.

The ink composition may be an inkjet ink composition. The ink composition may be a radiation curable inkjet ink composition such as a UV curable inkjet ink composition.

In another aspect the present invention provides a printed deposit formed from the ink composition of the invention. The printed deposit comprises a cross linked polymer formed from the amine functional vinyl ether compound having at least two vinyl ether groups and the monomer.

In this way the present invention provides an ink composition and/or printed deposit which provides reduced degradation of the non-wetting coating on the nozzle plate whilst maintaining low viscosity and good print properties such as toughness and adhesion to the substrate.

It has surprisingly been found that by providing multiple vinyl ether moieties and an amine moiety in the same compound the ability of the vinyl ether groups to attack the non-wetting coating on the nozzle plate is reduced or limited. It is also surprisingly found that the provision of multiple vinyl ether moieties and an amine moiety in the same compound provide good viscosity to the ink composition and good surface cure and mechanical properties to the cured film.

Without wishing to be bound by theory, it is proposed that the vinyl ether moieties and the amine moiety may provide a handle to crosslink into the polymer matrix as the ink cures. It is thought that this crosslinking improves toughness, adhesion and cure rate in the ink. It is also proposed that by combining the vinyl ether groups into the amine containing molecule, these groups are less able to attack the non-wetting coating on the nozzle plate whilst still acting to reduce the viscosity of the ink composition.

The ink composition is compatible with the components of a printer, for example an inkjet printer, and more particularly a drop on demand inkjet printer. The ink composition is suitable for application directly onto products and/or product packaging to achieve high quality images.

DE19602071 is directed to coatings and aims to solve problems associated with coating curing. DE19602071 proposes to use compounds having a (meth)acrylate and an amine in the coatings in order to provide the desired coating properties. The compounds also have at least one vinyl ether group. The viscosities of the coatings in DE19602071 are high, 500 mPa.s, which is in keeping with the purpose of the invention, to provide coating compositions that have such high viscosities. The compounds in DE19602071 are made by Michael addition of an amine vinyl ether compound to a (meth)acrylate compound.

Amine Functional Vinyl Ether Compound

The ink composition contains an amine functional vinyl ether compound having at least two vinyl ether groups.

The term vinyl ether refers to the chemical group $*\text{-OCHCH}_2$ wherein * denotes the point of attachment to the rest of the amine functional vinyl ether compound. The oxygen atom in the vinyl ether forms an ether functional group when attached to the rest of the amine functional vinyl ether compound. That is, there is not a carbonyl group bonded directly to the oxygen atom as this forms an ester functionality and is not within the scope of the term vinyl ether.

In some embodiments, the amine functional vinyl ether compound may have at least three or at least four vinyl ether functional groups.

The term “amine functional” used herein refers to the presence of an amine group in the same molecule as the vinyl ether. The term “amine” includes secondary and tertiary amines, that is, amines having two non-hydrogen substituents (i.e. NRR’H) or three non-hydrogen substituents (i.e. NRR’R”) respectively. The term “amine” used herein does not include amide groups.

The term “amine” as used herein does not include primary amines, that is, amines having only one non-hydrogen substituent (i.e. NRH_2). Without wishing to be bound by theory it is proposed that the presence of primary amines results in reactivity towards other monomers in the ink, such as acrylates, and this reactivity may cause viscosity and stability problems in the ink. Tertiary amines may be preferred due to increased stability.

In the amine functional vinyl ether compound the amine and the at least two vinyl ether groups are joined by linking groups. The amine functional vinyl ether compound may have any suitable linking groups provided there are at least two vinyl ether groups and an amine moiety in the same compound. Preferably, the linker groups are selected from alkyl, alkenyl, alkynyl, cycloalkyl, aminoalkyl (e.g. bisaminopropyl piperazine), glycol or polyglycol (e.g. polyethylene glycol or polypropylene glycol) groups or combinations thereof (e.g. an ester of a glycol ether).

The linking group may be formed from the groups present on the compounds used to synthesise the amine functional vinyl ether. For example, when 2-(2-vinylethoxy)ethyl acrylate (VEEA) is used to provide the vinyl ether group, part of the linker group is the ester of glycol ether derived from the VEEA skeleton after the acrylate of VEEA has reacted with an amine.

The amine functional vinyl ether may contain other functional groups, for example, may contain one or more groups selected from a hydroxyl group, an ether, a ketone, an amide, an ester or a combination thereof.

The amine functional vinyl ether compound may have at least two amine functional groups, for example at least 3, or at least 4 amine functional groups.

The amine functional vinyl ether compound may have at most 30 amine functional groups, for example at most 20, at most 10, at most 5, or at most 4 amine functional groups.

The amine functional vinyl ether compound may have a number of amine functional groups selected from a range of any of the above values. For example, the amine functional vinyl ether compound may have from 2 to 4 amine functional groups.

In this way, it is proposed that the multiple amine groups provide additional opportunity to cross link into the polymer as the ink cures and also additional reduction in the problem of oxygen inhibition.

Preferably, each of the amines in the amine functional vinyl ether compound is a secondary or tertiary amine.

In some cases, at least one of the amines in the amine functional vinyl ether compound is a tertiary amine. Preferably, each of the amines in the amine functional vinyl ether is a tertiary amine.

In some embodiments, the amine functional vinyl ether compound is a monomer. In some embodiments, the amine functional vinyl ether compound is an oligomer or polymer.

Suitable amine functional vinyl ethers for use in the inks of the invention include:

2-(2-vinyloxyethoxy)ethyl 3-[6-[bis[3-oxo-3-[2-(-vinyloxyethoxy)ethoxy]propyl]amino]hexyl-[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]propanoate;

2-(2-vinyloxyethoxy)ethyl 3-[2-[2-[2-[bis[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]ethoxy]ethoxy]ethyl-[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]propanoate;

2-(2-vinyloxyethoxy)ethyl 3-[3-[bis[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]propyl-[4-(dimethylamino)butyl]amino]propanoate;

2-(2-vinyloxyethoxy)ethyl 3-[4-hydroxybutyl-[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]propanoate;

2-(2-vinyloxyethoxy)ethyl-3-[4-(2-hydroxyethoxy)butyl-[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]propanoate; and

2-(2-vinyloxyethoxy)ethyl 3-[[3-[bis[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]-2-hydroxy-propyl]-[3-oxo-3-[2-(2-vinyloxyethoxy)ethoxy]propyl]amino]propanoate.

In some embodiments, the amine functional vinyl ether compound is a compound produced by Michael addition of an amine to an acrylate compound having a vinyl ether functional group. This type of reaction is often referred to as an aza-Michael addition, where aza refers to the use of an amine nucleophile. For example, the amine functional vinyl ether compound may be produced by an aza-Michael addition of a primary or secondary amine and 2-(2-vinylethoxy)ethyl acrylate (VEEA).

It is generally preferable for industrial products, particularly chemicals, to be available as consistent and controllable compositions. For example, in the case of ink compositions the components used in the ink need to consistently and controllably provide viable inks (e.g. inks with viscosities suitable for printing and that tolerate the printing process) and consistent printed deposits. The components making up the ink affect these properties and so consistent and controllable components are desirable.

The aza-Michael reaction is well known and has a well-established mechanism. Thus, the product of an aza-Michael reaction can be determined by the choice of starting materials and stoichiometry of the reaction. For example, to obtain an amine functional vinyl ether compound that is multifunctional in amine, the skilled person understands that the amine starting material may be selected from diamines or that a vinyl ether containing component may be selected so that it can react with two different amines (e.g. has two of more α,β-unsaturated carbonyl groups). Additionally, for example, to obtain an amine functional vinyl ether compound having multiple vinyl ether groups, the skilled person understands that the Michael acceptor may be selected to have multiple vinyl ether groups or that the amine component may be selected to react with two or more Michael acceptors containing a single vinyl ether group (e.g. the amine may be a primary amine).

In some embodiments, the amine functional vinyl ether compound is synthesised from an acrylate that is monofunctional in acrylate, or an amine that is monofunctional in amine. In this context, a primary amine is difunctional because it has the ability to react twice by Michael addition.

In this way, the amine functional vinyl ether compound may be produced with increased precision and consistency

In some embodiments, the amine functional vinyl ether compound is a monomer. In such cases, the monomer may be obtained by an aza-Michael reaction of a small molecule amine. The small molecule amine may be selected from: alkyl mono-amines (i.e. alkyl amines having only 1 amine group) such as ethylamine, propylamine, butylamine, diethylamine, dipropylamine, dibutylamine; alkyl di-amines (i.e. alkyl amine having only 2 amine groups) such as hexamethylene diamine; multifunctional amines such as N,N-dimethyldipropylenetriamine (DMAPAPA), 3-(diethylamino)propylamine (DEAPA),1,3-cyclohexanebis(methylamine), bisaminopiperazine; alcohol functional amines such as ethanolamine, 3-amino-1-propanol, 2-(2-aminoethoxy)ethanol, 1,3 diamino-2-propanol, 2-amino-1,3-propanediol; and vinyl ether functional amines such as amino propyl vinyl ether. Preferably, the small molecule amine is selected from hexamethylene diamine, N,N-dimethyldipropylenetriamine, 3-amino-1-propanol, 2-(2-aminoethoxy)ethanol and 1,3-diamino-2-propanol.

In some embodiments the amine functional vinyl ether is an oligomer or polymer. In such cases, the oligomer or polymer may be obtained by an aza-Michael reaction of an oligmeric or polymeric amine precursor. Suitable amine precursors include: amine terminated polyether oligomers or polymers such as are available from Huntsman as the Jeffamine range; polyethyleneimine polymers such as are available from BASF as the Lupasol range; or an amine terminated polymer produced from the reaction of multifunctional amine with multifunctional acrylate under conditions of excess amine. In the latter case the degree of excess will determine the molecular weight of the amine functional oligomer or polymer.

By choosing different amine functional starting oligomer or polymers (e.g. by selecting a polymer or oligomer containing polyether linkages) it is possible to manipulate the hydrophilic-hydrophobic character of the aminated vinyl ether that is synthesised.

Preferably, the amine functional vinyl ether compound is present at 35 wt % or less based on total weight of the ink composition, more preferably 30 wt % or less, more preferably 27 wt % or less and in some cases preferably 20 wt % or less. Preferably, the amine functional vinyl ether compound is present at 5.0 wt % or more based on total weight of the ink composition, preferably 10 wt % or more, and even more preferably 12 wt % or more. The amine functional vinyl ether compound may be present in an amount that is in a range with the upper and lower limits selected from the amounts described above. For example, the amine functional vinyl ether compound is present at 10 to 30 wt % based on total weight of the ink composition.

It is proposed that the amount of amine functional vinyl ether can affect the viscosity of the ink and so the amount of amine functional vinyl ether may be used to adjust the viscosity of the ink for a particular purpose.

The molecular weight of the amine functional vinyl ether compound is not particularly limited. The upper limit on the molecular weight may be determined based on the amount of the amine functional vinyl ether that can be used in a formulation whilst respecting the viscosity specification for a particular printing application. For example, in inks for use in flexo, screen, offset or intaglio printing, the amine functional vinyl ether compound may preferably have a molecular weight of at most 100,000. For inks for use in inkjet or gravure applications the amine functional vinyl ether compound may preferably have a molecular weight of at most 20,000, at most 5000, at most 3000, at most 1200 or at most 1000.

In some embodiments, the amine functional vinyl ether compound has a molecular weight of at least 150. For example, at least 250, at least 300, at least 350, at least 450 or at least 500.

In some embodiments, the amine functional vinyl ether compound has a molecular weight of at most 10,000. For example, at most 5000, at most 3000, at most 1200 or at most 1000.

The amine functional vinyl ether compound may have a molecular weight selected from a range of any of the above values. For example, the amine functional vinyl ether compounds may have a molecular weight from 400 to 5000.

It is proposed that amine functional vinyl ether compounds with the above molecular weights may provide particularly effective suppression of the degradation of the non-wetting coating that is applied to an inkjet print head nozzle plate.

In the case where the amine functional vinyl ether is an oligomer or a polymer, the molecular weight refers to the number average molecular weight.

Preferably the amine functional vinyl ether described herein has a viscosity of less than 1000 mPa.s, preferably less than 500 mPa.s, and more preferably less than 200 mPa.s at 25ºC.

Preferably the amine functional vinyl ether described herein has a viscosity of greater than 50 mPa.s, more preferably greater than 80 mPa.s, even more preferably greater than 100 mPa.s at 25 ºC.

The amine functional vinyl ether compound may have a viscosity selected from a range of any of the above values. For example, the amine functional vinyl ether has a viscosity of about 50 to 1000 mPa.s at 25ºC.

The viscosity of the amine functional vinyl ether may be measured using a rheometer such as the MCR302 from Anton Paar or using a viscometer such as a Brookfield DV- II+ viscometer.

Monomer

The ink composition contains a monomer. The monomer has at least one functional group that can undergo polymerization.

The monomer may be a radiation curable monomer, such as a UV curable monomer. The monomer may be a single monomer or may be a combination of two or more monomers.

The polymerizable functional group of the monomer may be an acrylate, methacrylate, maleate, fumarate, an acrylamide functional group or a mixture thereof. Preferably the polymerizable functional group is an acrylate.

The monomer may be mono functional or may be multifunctional such as di-functional. Preferably the monomer is di-functional.

Suitable mono-functional monomers include mono-functional acrylates, mono-functional acrylamides, mono-functional vinyl compounds, mono-functional methacrylates, mono-functional allyl ethers, mono-functional maleates, mono-functional fumarates, mono-functional methacrylamides or a mixture thereof.

Suitable monofunctional acrylates include caprolactone acrylate, cyclic trimethylolpropane formal acrylate, ethoxylated nonyl phenol acrylate, isodecyl acrylate, isooctyl acrylate, octyldecyl acrylate, alkoxylated phenol acrylate, tridecyl acrylate, isoamyl acrylate, stearyl acrylate, lauryl acrylate, octyl acrylate, decyl acrylate, isoamylstyl acrylate, isostearyl acrylate, 2-ethylhexyl-diglycol acrylate, 2-hydroxybutyl acrylate, butoxyethyl acrylate, ethoxydiethylene glycol acrylate, methoxydiethylene glycol acrylate, methoxypolyethylene glycol acrylate, methoxypropylene glycol acrylate, phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-acryloyloxyethylsuccinic acid, 2-acryloxyethylphthalic acid, 2-acryloxyethyl-2-hydroxyethyl-phthalic acid, lactone modified flexible acrylate, t-butylcyclohexyl acrylate or VEEA. VEEA may be added to the formulation or may be residual VEEA from synthesis of the aminated vinyl ether via the Michael addition route.

Suitable mono-functional acrylamides include acryloyl morpholine, N-isopropyl acrylamide, N-tert-butyl acrylamide, diacetone acrylamide.

Suitable multi-functional monomers may have two or more functional groups selected from an acrylate, maleate, fumarate or acrylamide functional group. Preferably the monomer is di-functional and more preferably contains two acrylate groups.

Suitable multi-functional acrylate monomers include hexanediol diacrylate (e.g. 1,6-hexanediol diacrylate), 3-methyl-1,5-pentanediyl diacrylate, di -trimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, ethoxylated pentaerythritol tetraacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, polyethylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, polypropylene glycol diacrylate, 1,4-butanediol diacrylate, 1,9-nonanediol diacrylate, neopentyl glycol diacrylate, dimethylol-tricyclodecane diacrylate, bisphenol A EO (ethylene oxide) adduct diacrylate, bisphenol A PO (propylene oxide) adduct diacrylate, hydroxypivalate neopentyl glycol diacrylate, propoxylated neopentyl glycol diacrylate, alkoxylated dimethyloltricyclodecane diacrylate and polytetramethylene glycol diacrylate, trimethylolpropane triacrylate, EO modified trimethylolpropane triacrylate, tri (propylene glycol) triacrylate, caprolactone modified trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerithritol tetraacrylate, ethoxylated pentaerythritol tetraacrylate, glyceryl propoxy triacrylate, or caprolactam modified dipentaerythritol hexaacrylate.

Preferably, the monomer is a multi-functional acrylate monomer such as a di-functional acrylate monomer. The di-functional acrylate monomer may be hexanediol diacrylate (HDDA, e.g. 1,6-hexanediol diacrylate), 3-methyl-1,5-pentanediyl diacrylate (MPDDA), dipropylene glycol diacrylate (DPGDA), neopentyl glycol diacrylate (NPGDA) or propoxylated neopentyl glycol diacrylate (PONPGDA). Preferably the di-functional acrylate monomer may be HDDA or MPDDA. MPDDA is also known as 3-methyl-1,5-pentanediol diacrylate.

Preferably, the monomer is present at 90 wt % or less based on total weight of the ink composition, preferably 85 wt% or less, and even more preferably 80 wt % or less. Preferably, the monomer is present at 40 wt % or more based on total weight of the ink composition, preferably 50 wt % or more or 55 wt% or more and even more preferably 65 wt % or more. The monomer compound may be present in an amount that is in a range with the upper and lower limits selected from the amounts described above. For example, the monomer may be present at 50 to 85 wt % based on total weight of the ink composition.

In some embodiments, the monomer has a molecular weight of at least 150. For example, at least 200, or at least 225.

In some embodiments, the monomer has a molecular weight of at most 1000. For example, at most 800, at most 500, or at most 300.

The monomer may have a molecular weight selected from a range of any of the above values. For example, the monomer may have a molecular weight from 100 to 500.

Oligomer

The ink compositions of the invention may also comprise a curable oligomer, such as a radiation curable oligomer (e.g. polyester acrylate, urethane acrylate, polyether acrylate or epoxy acrylate).

However, preferably the ink will contain no oligomeric curable material other than the amine functional vinyl ether compound when such is an oligomer.

Colourant

The ink composition and the printed deposit may comprise a colourant. The colourant is not particularly limited and any suitable colourant known in the art may be used.

The colourant may be a dye or a pigment. Preferably, the colourant comprises a pigment.

Examples of suitable yellow dyes include aryl or heteryl azo dyes having a coupling component such as a phenol, a naphthol, an aniline, a pyrazolone, a pyridone, or an open-chain active methylene compound; azomethine dyes having a coupling component such as an open-chain active methylene compound; methine dyes such as benzylidene dyes and monomethineoxonol dyes; quinone dyes such as naphthoquinone dyes and anthraquinone dyes; and other dye species such as quinophthalone dyes, nitro/nitroso dyes, acridine dyes, and acridinone dyes.

Examples of suitable magenta dyes include aryl or heteryl azo dyes having a coupling component such as a phenol, a naphthol, or an aniline; azomethine dyes having a coupling component such as a pyrazolone or a pyrazolotriazole; methine dyes such as arylidene dyes, styryl dyes, merocyanine dyes, and oxonol dyes; carbonium dyes such as diphenylmethane dyes, triphenylmethane dyes, and xanthene dyes; quinone dyes such as naphthoquinones, anthraquinones, or anthrapyridones; and condensed polycyclic dyes such as dioxazine dyes.

Examples of suitable cyan dyes include indoaniline dyes, indophenol dyes, and azomethine dyes having a coupling component such as a pyrrolotriazole; polymethine dyes such as cyanine dyes, oxonol dyes, and merocyanine dyes; carbonium dyes such as diphenylmethane dyes, triphenylmethane dyes, and xanthene dyes; phthalocyanine dyes; anthraquinone dyes; aryl or heteryl azo dyes having a coupling component such as a phenol, a naphthol, or an aniline; and indigo/thioindigo dyes.

When the colourant is a pigment, the pigment may be in the form of a dispersion in the composition. The pigment may be an inorganic or an organic pigment.

Preferably the pigment has an average particle size of less than 1 µm. The average particle size referred to here is the Z average particle size calculated using dynamic light scattering. This is the intensity weighted mean hydrodynamic size of the collection of particles.

For example, the inorganic pigment may be selected from titanium oxides such as titanium dioxide, iron oxide and carbon blacks produced by known processes, such as contact, furnace, and thermal processes.

For example, the organic pigments may be selected from azo pigments (including azo lake, insoluble azo pigment, condensed azo pigment, and chelate azo pigment), polycyclic pigments (for example, phthalocyanine , perylene, perinone, anthraquinone, quinacridone , dioxazine, thioindigo, isoindolinone, and quinophthalone pigments), dye-type chelate pigment (for example, basic dye-type chelate pigments and acid dye-type chelate pigment), nitro pigments, nitroso pigments, and aniline black.

Carbon blacks usable for black inks include carbon blacks manufactured by Mitsubishi Chemical Corporation, for example, No. 2300, No. 900, MCF 88, No. 33, No. 40, No. 45, No.52, MA 7, MA 8, MA 100, and No. 2200 B; carbon blacks manufactured by Columbian Carbon Co., Ltd., for example, Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255, and Raven 700; carbon blacks manufactured by Cabot Corporation, for example, Regal 400 R, Regal 330 R, Regal 660 R, Mogul L, Monarch 700, Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300, and Monarch 1400; and carbon blacks manufactured by Degussa, for example, Color Black FW 1, Color Black FW 2, Color Black FW 2 V, Color Black FW 18, Color Black FW 200, Color Black S 150, Color Black S 160, Color Black S 170, Printex 35, Printex U, Printex V, Printex 140 U, Special Black 6, Special Black 5, Special Black 4A, and Special Black 4.

Pigments for yellow inks include C.I. Pigment Yellow 1, C.I. Pigment Yellow 2, C.I. Pigment Yellow 3, C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 16, C.I. Pigment Yellow 17, C.I. Pigment Yellow 73, C.I. Pigment Yellow 74, C.I. Pigment Yellow 75, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 95, C.I. Pigment Yellow 97, C.I. Pigment yellow 98, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 114, C.I. Pigment Yellow 128, C.I. Pigment Yellow 129, C.I. Pigment yellow 138, C.I. Pigment Yellow 150, C.I. Pigment Yellow 151, C.I. Pigment Yellow

154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 180, C.I. Pigment Yellow 185, and C.I. Pigment Yellow 139.

Pigments for magenta inks include C.I. Pigment Violet 19, C.I. Pigment Red 5, C.I. Pigment Red 7, C.I. Pigment Red 12, C.I. Pigment Red 48 (Ca), C.I. Pigment Red 48 8 (Mn), C.I. Pigment Red 57 (Ca), C.I. Pigment Red 57 : 1, C.I. pigment Red 112, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 168, C.I. Pigment Red 184, C.I. Pigment Red 202, C.I. Pigment Red 176, C.I. Pigment Red 254, C.I. Pigment Red 255, C.I. Pigment Red 272 or C.I. Pigment Red 254.

Pigments for orange inks include C.I. Pigment Orange 64, and C.I. Pigment Orange 73.

Pigments for cyan inks include C.I. Pigment Blue 1, C.I. Pigment Blue 2, C.I. Pigment Blue 3, C.I. Pigment Blue 16, C.I. Pigment Blue 22, C.I. Pigment Blue 60, C.I. Vat Blue 4, C.I . Vat Blue 60, C.I. Pigment Blue 15:2, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4,

Pigments for green inks include C.I. Pigment Green 36, and C.I. Pigment Green 7.

Pigments for violet inks include C.I. Pigment Violet 23 and C.I. Pigment Violet 37.

Preferably, the organic pigment is selected from C.I. Pigment Red 122, C.I. Pigment Red 176, C.I. Pigment Red 254, C.I. Pigment Red 255, C.I. Pigment Red 272, C.I. Pigment Violet 19, C.I. Pigment Orange 64, C.I. Pigment Orange 73, C.I. Pigment Yellow 83, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 151, C.I. Pigment Yellow 154, Pigment Yellow 155, C.I. Pigment Blue 15:2, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Green 7, C.I. Pigment Violet 23 and C.I. Pigment Violet 37.

Preferably the colourant is present in between 0.5 to 20 wt % based on total weight of the ink composition, more preferably 1.0 to 10 wt %, and most preferably 1.5 to 4 wt % based on total weight of the ink composition.

Preferably, the colourant is present in less than 20 wt % based on total weight of the ink composition, more preferably less than 10 wt % and even more preferably less than 5 wt %. Preferably, the colourant is present in greater than 0.5 wt % based on total weight of the ink composition, preferably greater than 1.0 wt %, and even more preferably greater than 1.5 wt %. The colourant may be present in an amount that is in a range with the upper and lower limits selected from the amounts described above.

In this way the ink composition may have the desired opacity and colour.

Initiators

The curable ink composition may comprise an initiator. The initiator may be a thermal initiator or a photoinitiator, preferably the initiator is a photoinitiator.

The term initiator refers to a compound that undergoes a reaction due to an external stimulus producing a reactive species such as a radical. The external stimulus may be thermal radiation, actinic radiation, for example UV or visible radiation, or an electron beam. The reactive species reacts with one or more of the monomers to initiate the polymerization reaction.

The term photoinitiator refers to a compound that undergoes a photoreaction on absorption of light, producing at least one reactive species such as a radical. The external stimulus may be visible light or UV radiation, preferably the external stimulus is UV radiation. The reactive species produced reacts with one or more of the monomers to initiate the polymerization reaction.

The photoinitiator may provide this function when irradiated with light having a wavelength within the range of 450 to 200 nm (i.e. UV radiation). This may mean that the photoinitiator has light absorption characteristics in the entire wavelength range of 450 to 200 nm.

Photoinitiators are well known in the art. Suitable photoinitiators may be selected from: α-hydroxy ketones (such as 1-hydroxycyclohexyl-phenyl ketone or 2-hydroxy-2-methylpropiophenone); difunctional α-hydroxy ketones (such as 2-hydroxy-1-(4-(4-(2-hydroxy-2-methylpropionyl)benzyl)phenyl)-2-methylpropan-1-one, 2-hydroxy-1-[4-[[4-(2-hydroxy-2-methyl-propanoyl)phenyl]methyl]phenyl]-2-methyl-propan-1-one or the photoinitiator sold by IGM resins under the product name Esacure One); α-amino ketones; phosphine oxides (such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide, or ethyl phenyl(2,4,6-trimethylbenzoyl)phosphinate); benzophenones; ketosulphones; thioxanthones (such as ITX, DETX or Omnipol TX); ketocoumarins; benzil ketals; benzoylformate esters; or a mixture thereof. The photoinitiator may be selected from the list published by EuPIA as suitable for food contact materials.

Preferably, the photoinitiator is selected from bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, difunctional α-hydroxy ketones, ketosulphones (such as Esacure 1001M), polymeric thioxanthones and a mixture thereof. More preferably, the photoinitiator is a mixture of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (such as Omnirad 819), a difunctional α-hydroxy ketones (such as Omnirad 127 or Esacure KIP160), a polymeric thioxanthone (such as Omnipol TX), a ketosulphone (such as Esacure 1001M) and ethyl phenyl(2,4,6-trimethylbenzoyl)phosphinate.

Preferably, the total amount of the photoinitiator is 20 wt % or less based on total weight of the ink composition, more preferably 15 wt % or less and even more preferably 10 wt % or less.

Preferably, the total amount of the photoinitiator is 1 wt % or more based on total weight of the ink composition, preferably 3 wt % or more, and even more preferably 5 wt % or more.

The total amount of the photoinitiator may be an amount that is in a range with the upper and lower limits selected from the amounts described above. For example, the total amount of the photoinitiator is 5 to 10 wt % based on total weight of the ink composition.

In alternative embodiments, the ink compositions of the invention are substantially free from photoinitiator. In such cases, the ink composition may be cured by electron beam.

Solvents

The ink composition may comprise organic solvent such as ethanol, methyl ethyl ketone or the like. The organic solvent may be used to reduce the viscosity of the ink composition and aid solubility of the photoinitiators.

However, preferably the ink composition is substantially free from organic solvent.

The ink composition may comprise water. However, preferably the ink composition is substantially free from water.

Additives

The ink composition and/or the printed deposit may contain additional components, such as are common in the art.

Preferably, the ink composition and/or the printed deposit may further comprise one or more stabilisers, binders, humectants, wetting aids (e.g. surfactants), defoamers, slip aids (e.g. waxes), conductivity additives, tackifiers, adhesion promotors, dispersants, preservatives, biocides and mixtures of two or more thereof.

Stabilisers

The ink composition and/or the printed deposit may further comprise a stabiliser. It is proposed that, in some cases the jetting performance of an inkjet ink is dependent on its viscosity. Undesired free radical polymerisation, for example of the acrylate or vinyl ether groups, can lead to a viscosity increase. A stabiliser may be used to prevent undesired free radical polymerisation, for example the stabiliser may act as a polymerisation inhibitor to avoid even low levels of free radical polymerisation in the ink during storage or before use.

Suitable stabilisers include p-methoxy phenol (MEHQ), butylated hydroxy toluene (BHT), quinone methide, cupferron-Al, and TEMPO. For ease of handling, stabilisers are often supplied as solutions in monomer. Preferably a solution containing multiple stabilisers is used, for example Genorad 26 which is available from Rahn.

Preferably, each stabiliser is present at from 0.005 to 0.5 wt % based on the active component expressed as a percentage of the total weight of the ink composition, more preferably at from 0.01 to 0.3 wt% based on the total weight of the ink composition.

Binders

A binder, such as a binder resin, may be present in the ink composition and/or the printed deposit.

The binder comprises one or more polymers. The binder may be selected from any suitable binder, for example, suitable binders include polyamide resins, polyurethane resins, rosin ester resins, acrylic resins, polyvinyl butyral resins, polyesters, phenolic resins, vinyl resins, polystyrene/polyacrylate copolymers, cellulose ethers, cellulose nitrate resins, polymaleic anhydrides, acetal polymers, polystyrene/polybutadiene copolymers, polystyrene/polymethacrylate copolymers, sulfonated polyesters, ketone aldehyde condensation resins, polyhydroxystyrene resins and polyketone resins and mixtures of two or more thereof.

Preferably, the binder is selected from cellulosic resins, acrylic resins, vinyl resins, polyamides, polyesters, polyvinyl (e.g. polyvinyl butyral (PVB)), and polyurethanes. More preferably, the binder is a cellulosic resin. Even more preferably, the cellulosic resin is cellulose acetate butyrate.

Preferably, the binder has a molecular weight, such as a weight average molecular weight (Mw) between 500 and 50,000, more preferably between 1,500 and 50,000, more preferably between 10,000 and 50,000 and even more preferably between 15,000 and 50,000. Preferably, the binder has a molecular weight, such as a weight average molecular weight (Mw) of at least 500, more preferably at least 1,500, more preferably at least 10,000 and even more preferably at least 15,000. Preferably, the binder has a molecular weight, such as a weight average molecular weight (Mw) less than 50,000. The binder has a molecular weight, such as a weight average molecular weight (Mw) that is in a range with the upper and lower limits selected from the amounts described above.

Humectants

The ink composition and/or the printed deposit may further comprise a humectant. The humectant may be reactive or non-reactive. It is generally required that non-reactive humectants are removed from the printed deposit by forced drying in order to achieve a tack free printed deposit.

Suitable non-reactive humectants include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,4-cyclohexanedimethanol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,2-propanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, glycerol, 1,2,6-hexanetriol, sorbitol, 2-pyrrolidone, 2-propanediol, butyrolactone, and 1,2,4-butanetriol and mixtures of two or more thereof. Preferably the humectant is selected from a group consisting of glycerol, polypropylene glycol and mixtures of two or more thereof.

Suitable reactive humectants include polyethylene glycol acrylates and diacrylates, and highly ethoxylated monomers such as ethoxylated trimethylol propane triacrylate.

The ink composition may comprise up to 30% by weight of humectants based on the total weight of the composition. More preferably, the ink composition comprises up to 20% by weight of humectants based on the total weight of the composition.

Wetting aids

The ink composition and/or the printed deposit may further comprise a wetting aid, which is typically a surface active material (surfactant).

Suitable surfactants include anionic, cationic or non-ionic surfactants and mixtures of two or more thereof. Non-limiting examples of anionic surfactants include alkyl sulphate, alkylaryl sulfonate, dialkyl sulfonate, dialkyl sulphosuccinate, alkyl phosphate and polyoxyethylene alkyl ether sulphate. Non-limiting examples of cationic surfactants include alkylamine salt, ammonium salt, alkylpyridinium salt and alkylimidazolium salt. Non-limiting examples of non-ionic surfactants include polyoxyethylene alkyl ether, polyoxyethylene alkylaryl ether, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, glycerine fatty acid ester, a fluorine-containing non-ionic surfactant and a silicon-containing non-ionic surfactant, such as a polyether siloxane copolymer. Mixtures of two or more surfactants may be used.

Preferably the wetting aid is a silicone based surfactant, for example a silicone polyether acrylate wetting agent such as TEGO Rad 2300, BYK-333, BYK-377, BYK-378, or a mixture thereof.

The ink composition may comprise up to 5% by weight of surfactant based on the total weight of the composition. More preferably, the ink composition comprises up to 2 wt % of surfactant based on the total weight of the composition.

Defoamer

The ink composition and/or the printed deposit may further comprise a defoaming agent, for example, may contain BYK 1790.

The surface active nature of some wetting agents can cause excessive foaming of low viscosity inks and the use of a defoamer can prevent such issues.

Slip aid

The ink composition and/or the printed deposit may further comprise a slip aid.

The slip aid may be a wax, or it may be a surface active material such as a silicone based surfactant, for example Tego Glide 432 or Tego Glide 410.

If the printing process will tolerate the presence of particles then a particulate wax such as a polyethylene or PTFE wax, or a copolymer may be used. Alternatively the wax may be of the fatty amide type, such as erucamide or oleamide.

The wax may be chosen such that its melting point is lower than the temperature of application. The rub and scuff properties of the printed film may be enhanced by the use of a wax.

Conductivity Additives

The ink composition and/or the printed deposit may further comprise a conductivity additive. The conductivity additive may be any organic salt known in the art.

Conductivity additives for ink compositions are well-known in the art.

Preferably, the organic salt is selected from quaternary ammonium or phosphonium salts. For example, the organic salt may be selected from tetraethylammonium chloride, tetraethylammonium bromide, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium acetate, tetrabutylammonium nitrate, tetrabutylammonium tetrafluoroborate, tetrabutylammonium hexafluorophosphate, tetrabutylphosphonium chloride and tetrabutylphosphonium bromide. A preferred salt is tetrabutylammonium bromide,

Preferably, the conductivity additive is present at from 0.1 to 5 wt % based on total weight of the ink composition.

Tackifier

The ink composition and/or the printed deposit may further comprise a tackifier.

Suitable tackifiers include resins such as rosins, terpenes and modified terpenes, aliphatic, cycloaliphatic and aromatic resins, terpene phenolic resins and silicone or mineral oils. Preferably the tackifier is a terpene phenolic resin and/or an ester of hydrogenated rosin. Most preferably the tackifier is a terpene phenolic resin.

The ink composition may comprise from 0.3 to 20 % by weight of tackifier based on the total weight of the composition. Preferably the radiation curable inkjet inks of this invention are substantially free from tackifier.

Adhesion Promoter

The ink composition and/or the printed deposit may further comprise an adhesion promoter.

An adhesion promotor is a substance which acts to promote adhesion of the ink composition to a substrate.

Suitable adhesion promotors are titanium phosphate complex, titanium acetylacetonate, triethanolamine zirconate, zirconium citrate, zirconium propanoate, organosilicon, polyketones binders, polyesters binders, or a ketone condensation resin.

Preferably the adhesion promoter is a titanium phosphate complex or a ketone condensation resin. More preferably, the adhesion promotor is a ketone condensation resin.

Dispersant

The ink composition and/or the printed deposit may further comprise a pigment dispersant. The dispersant is typically added at the pigment milling stage to stabilise the particles against subsequent aggregation.

The dispersant may be any suitable dispersant and may be selected from the polyester, polyurethane or polyacrylate type. Preferably, the dispersant is in the form of a high molecular weight block copolymer.

Suitable dispersants are available from BYK (for example Bykjet 9151 and 9152), Lubrizol (for example Solsperse 35000, 39000 and 88000) and BASF (for example EFKA 4701, 4703 and 4731).

The ink composition may comprise from 0.3 to 10 % by weight of dispersant based on the total weight of the composition. More preferably, the ink composition comprises from 0.7 to 7 % by weight of dispersant based on the total weight of the composition.

Preservatives

The ink composition and/or the printed deposit may further comprise a preservative.

Suitable preservatives include sodium benzoate, benzoic acid, sorbic acid, potassium sorbate, calcium sorbate, calcium benzoate, methylparaben and mixtures of two or more thereof. The preferred preservative is sodium benzoate.

The ink composition may comprise up to 2% by weight of preservative based on the total weight of the composition. More preferably, the ink composition comprises up to 1% by weight of preservative based on the total weight of the composition.

Biocides

The ink composition and/or the printed deposit may further comprise a biocide, for example Nipacide BIT 20 or Proxel XL2 or Proxel GXL.

Types of Packaging

The present disclosure further provides a method for printing images on a substrate comprising directing a stream of droplets of any of the embodiments of the ink composition of the invention onto a substrate and drying the ink droplets, thereby printing images on a substrate. Preferably, the ink is dried by the application of a suitable radiation source, which may be actinic radiation in the form of ultra violet or visible light, or may be an electron beam. The drying may be referred to as curing in these cases. Preferably, an inkjet printer is used in the method, more preferably a drop on demand inkjet printer is used in the method.

Any suitable substrate may be printed in accordance with the invention. The ink composition of the present invention is suitable for printing on both porous and non-porous materials, for example, substrates which are widely used for packaging of both food and non-food products~~.~~

Each of the methods of printing referred to above may be applied to any suitable article.

Examples of suitable substrates that make up the articles include glass, metal, laminate, ceramic, plastic, cardboard, and/or paper. Some preferred substrates include paper, LDPE, HDPE, polypropylene, PET, nylon, PVC, PVdC, aluminium or steel.

Each of the substrates may be in any suitable form such as in the form of bottles or containers, plates, rods or cylinders.

Examples of suitable articles include metalized cans, plastic pots, retort pouches, labels and flexible plastic films.

Methods and Uses

The present disclosure provides a method for printing markings on a substrate. The ink compositions of the invention may be suitable for radiation curing and may be printed using an inkjet printer, the method comprising the steps of directing a stream of droplets of the ink composition to a substrate and optionally curing the printed ink composition for example by treating the printed ink composition with UV radiation.

The ink compositions are formulated by combining the components using methods known in the art.

The curing process may be carried out by the application of thermal radiation, actinic radiation, for example UV or visible radiation, or an electron beam. Preferably the curing process is carried out by treating the printed ink composition with UV radiation.

The inkjet printer may be a thermal inkjet printer (i.e. a TIJ printer), a continuous inkjet printer (i.e. a CIJ printer) or a drop on demand inkjet printer (i.e. a DOD printer).

Preferably, the inkjet printer is a drop on demand inkjet printer, such as a piezoelectric drop on demand inkjet printer. In some preferable cases the inks are applied to the substrate using a high resolution drop on demand printer capable of emitting a range of droplet sizes below 20 pl volume.

Once applied to the substrate, the inks of the current invention may be cured. The curing process promotes the polymerization of the monomers in the ink composition to provide a printed deposit. The curing process may be initiated by an initiator.

The curing process may be a UV curing process. In such cases, the initiator may be a photoinitiator. The UV curing process may comprise a single application of UV radiation or multiple applications of UV radiation. In some cases, the UV curing process comprises two applications of UV radiation.

In some cases, the first (or only) application of UV radiation is provided by an LED. The LED preferably emits within the range 365 nm and 405 nm.

In other cases, the first (or only) application of UV radiation is provided by a mercury arc lamp such as an iron doped mercury arc lamp.

Preferably, the first application of UV radiation provides a dose of 395 nm light delivered at from 20 to 500 mJ/cm^2, and more preferably at from 50 to 200 mJ/cm^2 (measured as UVA2 using an EIT Power Puck).

Preferably, the first application of UV radiation occurs immediately after printing, for example using an LED positioned immediately adjacent to the print head. In this way, the ink is at least partially cured immediately after printing and further spreading of the ink across the substrate is prevented.

In some cases, the first application of UV radiation is sufficient to cure the ink.

In other cases, additional applications of UV radiation are required. This is particularly the case at high printing speeds, for example, print speeds up to 50 m/min or more. In these cases, the additional application of UV radiation is preferably provided by a mercury arc source. For the additional application of UV radiation the dose of UVA is preferably from 30 to 1000mJ/cm^2 and more preferably from 50 to 300mJ/cm^2 (measured with an EIT Power Map).

In a further embodiment, printing is carried out using a multi-pass inkjet printer. In this case, a UV light source, preferably an LED, is mounted on the printhead carriage. In this way, the UV light may be applied after each successive row of printing.

Advantageously, using the compositions and methods described herein overcomes and/or mitigates at least some of the problems described above, providing an improved quality print.

Substrate

The present disclosure provides a method for printing markings on a substrate. Any suitable substrate may be printed in accordance with the invention.

Examples of suitable substrates include porous substrates such as uncoated paper, semi-porous substrates such as aqueous coated paper, clay coated paper, silica coated paper, UV overcoated paper, polymer overcoated paper, and varnish overcoated paper, and non-porous substrates such as hard plastics, polymer films, polymer laminates, metals, metal foil laminates, glass, and ceramics. The paper substrates may be thin sheets of paper, rolls of paper, or cardboard. Plastics, laminates, metals, glass, and ceramic substrates may be in any suitable form such as in the form of bottles or containers, plates, rods, cylinders, etc.

In many cases the substrate will be a plastic film, paper or paperboard.

Suitable examples of plastic films include films comprising polyethylene, polypropylene, polyester, polyamide, PVC, polylactic acid, or cellulosic films. The plastic film may be pretreated or coated, for example to improve the adhesion of the inks or to render it more suitable for the application in question.

Metallic films such as those used for lidding applications, glass and ceramics may also be printed.

Definitions

As used herein the term “printed deposit” refers to the ink composition after it has been printed onto a suitable substrate. That is the ink composition of the present invention wherein at least some of the solvent, if present, has evaporated.

As used herein the term “ink composition” includes an ink composition suitable for use in any kind of printing, for example in inkjet printing. The ink composition is typically in the form of a liquid, and typically a solution.

As used herein the term “polymer” refers to any substance having a repeat unit and includes: polysaccharides and their derivative for example cellulose and its derivatives; addition polymers such as acrylic resins or polyvinyl resins; condensation polymers, for example polyurethanes, polyamide and polyesters; and co-polymers wherein the repeat unit is formed of two or more different compounds, for example of styrene and maleic anhydride.

Other Preferences

Each and every compatible combination of the embodiments described above is explicitly disclosed herein, as if each and every combination was individually and explicitly recited.

Various further aspects and embodiments of the present invention will be apparent to those skilled in the art in view of the present disclosure.

“and/or” where used herein is to be taken as specific disclosure of each of the two specified features or components with or without the other. For example “A and/or B” is to be taken as specific disclosure of each of (i) A, (ii) B and (iii) A and B, just as if each is set out individually herein.

Unless context dictates otherwise, the descriptions and definitions of the features set out above are not limited to any particular aspect or embodiment of the invention and apply equally to all aspects and embodiments which are described.

Certain aspects and embodiments of the invention will now be illustrated by way of example and with reference to the figures described above.

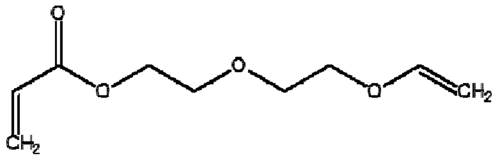
Examples

The following non-limiting examples further illustrate the present invention.

All commercial chemicals were used as bought from the suppliers unless otherwise stated.

2-(2-vinylethoxy)ethyl acrylate (VEEA) was obtained from Nippon Shokubai:

VEEA



Jeffamine EDR148, an amine functional polyether, was obtained from Huntsman.

BHT (2,6-di-tert-butyl-p-cresol) was obtained from IGM resins under the tradename Omnistab BHT

Diethylamine was obtained from Sigma Aldrich

Hexamethylene diamine was obtained from Sigma Aldrich

DMAPAPA (N,N Dimethyldipropylenetriamine) was obtained from Sigma Aldrich

Lupasol FG(polyethyleneimine) was obtained from BTC

3-amino-1-propanol was obtained from Sigma Aldrich

2-(2-aminoethoxy) ethanol was obtained from Sigma Aldrich

1,3 diamino-2-propanol was obtained from Sigma Aldrich

3-methyl-1,5-pentanediyl diacrylate (MPDDA) was obtained from Sartomer under the tradename SR341

Hexanediol diacrylate (HDDA) was obtained from Sartomer under the tradename SR238

Omnirad 819 (phosphine oxide photoinitiator), Omnirad TPO (phosphine oxide photoinitiator) and Esacure 1001M (ketosulphone photoinitiator) were obtained from IGM resins

Tegorad 2300 (silicone polyether acrylate) was obtained from Evonik industries

Genorad 26 (polymerisation inhibitor blend) was obtained from Rahn

Pigment Violet 19 was obtained from Clariant

Pigment blue 15:4 was obtained from BASF

Diethyleneglycol divinyl ether (DVE-2) was obtained from BASF

Aminopropyl vinyl ether was obtained from BTC

CN381 (amine modified polyether acrylate) was obtained from Sartomer

Ebecryl LEO10552 (amine modified polyether acrylate) was obtained from Allnex

Genomer 5275 (acrylated oligoamine resin) was obtained from Rahn

FTIR was carried out using a Thermo Scientific iS10 spectrophotometer operating with a diamond ATR crystal.

Print samples were created using a K control coater from RK PrintCoat Instruments using an 8µm Kbar. The substrate was BJ995, a paper label substrate, from Avery Dennison.

The prints were cured on a laboratory slider which allows the sample to be transported under the UV lamps at a speed which is representative of press operation. The LED lamp was a Phoseon FP300 395nm LED rated at 20W/cm^2 and the arc lamp was a Baldwin CoolArc rated at 240W/cm and operating with an iron doped bulb.

Viscosity was measured using a 1° 50 mm diameter cone and plate and a shear rate of 10s^{-1} on an Anton Paar MCR302 rheometer at 25 °C.

^1H NMR measurements were carried out on a on a DCH Cryoprobe Spectrometer at 500MHz. Sample were prepared in $CDCl_3$.

The surface cure of the print samples produced by the above method was evaluated using the “thumb-twist” test. This method assigns a value of 1 to 5 to a sample after the test, depending on the degree of curing, where 1 would indicate poor surface cure and 5 excellent. The test is performed by pressing the thumb firmly on the surface of the cured film and twisting the thumb. The surface of the ink film is then assessed for deformation, or film damage. Lighter pressure or a simple finger drag is performed to differentiate samples with little or no surface cure. The tests were scored according to the following criteria:

Score	Description
5	no visible mark left
4	surface smudges with thumb twist
3	surface smudges running finger over print
2	"fingerprint" left when touching surface
1	surface completely uncured

Adhesion of print samples produced by the above method was tested according to according to ISO2409 and using an Elcometer 107 Cross Hatch test kit. Tape pulls were made using two different tapes, the ISO2409 tape supplied by Elcometer and Scotch Magic tape from 3M. The reported scores are the % of ink remaining on the substrate after the tape pull.

Scratch of print samples produced by the above method was tested by rubbing the end of a fingernail backwards and forwards over the edge of the print so that any uncured material would be smeared onto the adjacent blank substrate. The tests were scored according to the following criteria:

Score	Description
5	minimal damage
4	visible mark left on the surface of the print
3	significant mark on surface or some transfer to blank paper
2	some removal to leave white patches or visible thinning of the film
1	significant removal from the substrate

MEK rub resistance was tested by wiping a cotton bud soaked in MEK repeatedly over the surface of the cured print. The result was recorded as the number of double rubs (there and back) until the first appearance of white spots of substrate from which the film had been totally removed. In cases where the surface cure was poor the surface layer is removed by the MEK so that the colour of the print becomes visibly weaker. Such results are recorded as ‘thins’ in the results table, and do not represent acceptable performance.

Nozzle plate wetting was tested by cutting strips of nozzle plate material coated with a non-wetting coating and immersion of half of the strip into each sample ink formulation. The strip was then removed from the ink formulation, allowed to drain for around 5 seconds and then placed on a flat surface. A photograph was taken of the strip at this stage to show the dewetting performance after a single immersion in the ink formulation. The nozzle plate strip were then re-immersed in the ink formulation and the immersed strip and ink formulation were placed in an oven at 60 °C for 2 weeks. This prolonged heating is used to mimic longer term exposure to the ink formulations. After this, each of the samples was removed from the oven and allowed to cool to room temperature. The immersed strip was removed from the ink formulation, allowed to drain for around 5 seconds and then placed on a flat surface. A second photograph is taken of the strip at this stage to show the dewetting performance after heating in the oven. Ink formulations were categorised acceptable if the ink reticulates off the nozzle plate surface and does not form a continuous film on the strip when tested after heating in the oven. Ink formulations were categorised as not acceptable if the ink does not reticulate off the nozzle plate surface and the ink forms a continuous film on the strip when tested after heating in the oven. Examples of this categorisation can be seen in Figure 1. The results of Figure 1b show acceptable tolerance of the nozzle plate coating by the inks. The results of Figure 1a show unacceptable tolerance of the nozzle plate coating resulting in increased wetting of the substrate after immersion.

Example 1 - Synthesis of Amine Functional Vinyl Ethers

Example amine functional vinyl ethers were synthesized via an aza-Michael addition of 2-(2-vinyloxethoxy) ethyl acrylate (VEEA) and primary or secondary amines. The amounts and procedure for each example amine are provided below.

Reaction of the primary amines proceeds readily, yielding secondary amines which are also reactive towards acrylates; the second reaction is more difficult to force to completion and typically requires that the reaction mix is held at a temperature between 60 and 120°C for several hours.

Reaction progress may be monitored by removing small samples and testing for infrared absorption at 1323cm^{-1} and 1408cm^{-1}. The 1323cm^{-1} absorption is due to the vinyl ether functionality which is not consumed in the reaction. Absorption at 1408cm^{-1} indicates the presence of acrylate. The stoichiometry in some cases is set up so that the acrylate functionality will be fully consumed at the point when the reactions are complete.

It is desirable to add a small amount of stabiliser to guard against gelation which can occur when the reaction mixture is heated. Suitable stabilisers include butyl hydroxy toluene (BHT), 4-Methoxyphenol, Tris(N-hydroxy-N-nitrosophenylaminato-O,O')aluminium, 2,6-bis(1,1-dimethylethyl)-4-(phenylenemethylene)cyclohexa-2,5-dien-1-one and triphenyl phosphite. BHT is used in the preparation of the example amines.

Comparative Amine 1

111.6g VEEA (0.6 equivalents) and 0.2g BHT stabiliser were heated to 72°C in a 500ml round bottomed flask fitted with a simple ascending condenser and equipped with a magnetic stirrer. 62.0ml diethylamine (0.6 equivalents) was injected in two 31.0ml aliquots, each of which caused a small exotherm. After the second exotherm had subsided the temperature was raised to 80°C and maintained for a further 6 hours, after which the reaction mix was allowed to cool to room temperature. A clear brown liquid product was obtained. 1H-NMR (500MHz, CDCl3) δ 6.48 (dd, J=14.3, 6.8Hz, 1H), 4.23 (t, J=4.8Hz, 2H), 4.18 (dd, J=14.3,2.2Hz, 1H), 4.00 (dd, J=6.8, 2.2Hz, 1H), 3.81-3.89 (m, 2H), 3.69-3.77 (m, 4H), 2.79 (t, J= 7.4Hz, 2H), 2.45-2.53 (m, 6H), 1.01 (t, J=7.2Hz, 6H); HRMS [M+H]+ calculated for $C_{13}H_{25}O_4N$ 260.1856 ; found 260.1855.

Example Amine 1

121.0g VEEA (0.65 equivalents) and 0.2g BHT stabiliser were heated to 70°C in the same apparatus as Comparative Amine 1. A total of 18.9g hexamethylene diamine (0.16 equivalents) was added as a melt in two approximately equal aliquots, each of which caused a small exotherm. After the second exotherm had subsided, stirring was maintained for a further 6 hours during which time the temperature was progressively raised to 100°C. 1H-NMR (500MHz, $CDCl_3$) δ 6.48 (dd, J=14.3, 6.8Hz, 4H), 4.22 (t, J=4.22Hz, 8H), 4.18 (dd, J=14.3, 2.1Hz, 4H), 4.01 (dd, J=6.8, 2.1Hz, 4H), 3.81-3.86 (m, 8H), 3.69-3.77 (m, 16H), 2.76 (t, J=7.3Hz, 8H), 2.46 (t, J= 7.3Hz, 8H), 2.38 (t, J=7.4Hz, 4H), 1.35-1.43 (m, 4H), 1.20-1.25 (m, 4H); HRMS [M+H]+ calculated for $C_{42}H_{72}O_{16}N_2$ 861.4955 ; found 861.4938.

Example Amine 2

111.6g VEEA (0.6 equivalents) and 0.1g BHT stabiliser were heated to 77°C in the same apparatus as example Amine 1. 22.2ml Jeffamine EDR148 (0.15 equivalents) was injected in two 11.1ml aliquots, each of which caused a small exotherm. After the second exotherm had subsided the temperature was maintained at 80°C for a further 6.5 hours. 1H-NMR (500MHz, $CDCl_3$) δ 6.48 (dd, J14.3, 6.8Hz, 4H), 4.22 (t, J4.8Hz, 8H), 4.18 (dd, J=14.3, 2.2Hz, 4H), 4.00 (dd, J=6.8,2.2Hz, 4H), 3.81-3.85 (m, 8H), 3.68-3.74 (m, 16H), 3.55 (s, 4H), 3.50 (t, J=6.4Hz, 4H), 2.81 (t, J=7.2Hz, 8H), 2.65 (t, J=6.4Hz, 4H), 2.47 (t, J=7.2Hz, 8H); HRMS [M+H]+ calculated for $C_{42}H_{72}O_{18}N_2$ 893.4853; found 893.4836

Example Amine 3

124.1g VEEA (0.67 equivalents) and 0.2g BHT stabiliser were heated to 70°C in the same apparatus as example Amine 1. A total of 40.1ml DMAPAPA (0.22 equivalents) was injected in two equal aliquots, each of which caused a small exotherm. After the second exotherm had subsided the temperature was maintained at 80°C for a further 4.5 hours. 1H-NMR (500MHz, $CDCl_3$) δ 6.47 (dd, J=14.3, 6.8Hz, 3H), 4.21 (t, J=4.8Hz, 6H), 4.17 (dd, J=14.3, 2.2Hz, 3H), 3.99 (dd, J=6.8, 2.2Hz, 3H), 3.81-3.84 (m, 6H), 3.68-3.73 (m, 12H), 2.74 (td, J=7.3, 1.7Hz, 6H), 2.44 (td, 7.3,3.4Hz, 6H), 2.34-2.42 (m, 6H), 2.22 (t, J=7.4Hz, 2H), 2.18 (s, 6H), 1.49-1.59 (m, 4H); HRMS [M+H]+ calculated for $C_{35}H_{63}O_{12}N_3$ 718.4485; found 718.4473.

Example Amine 4

148.5g VEEA (0.80 equivalents) and 0.25g BHT stabiliser were heated to 70°C in the same apparatus as example Amine 1. A total of 29.13ml Lupasol FG (0.04 equivalents) was injected in two approximately equal aliquots, each of which caused a small exotherm. After the second exotherm had subsided the temperature was maintained at 80°C for a further 7.0 hours. 1H-NMR (500MHz, $CDCl_3$) δ 6.48 (dd, J=14.3, 6.8Hz, 1H), 4.21-4.24 (m, 2H), 4.19 (dd, J=14.4, 1.8Hz, 1H), 4.01 (d, J=6.7, 1H), 3.81-3.87 (m, 2H), 3.67-3.77 (m, 4H), 2.74-2.82 (m, 2H), 2.44-2.53 (m, 6H).

Example Amine 5

130.34g VEEA (0.70 equivalents) and 0.23g BHT stabiliser were heated to 74°C in the same apparatus as example Amine 1. A total of 26.8ml 3-amino-1-propanol (0.35 equivalents) was injected in two approximately equal aliquots, each of which caused a small exotherm. After the second exotherm had subsided the temperature was maintained at 85°C for a further 7.0 hours. 1H-NMR (500MHz, $CDCl_3$) δ 6.48 (dd, J=14.3, 6.8Hz, 2H), 4.24 (tt, J=4.8, 1.2Hz, 4H), 4.18 (dd, J=14.3, 2.2Hz, 2H), 4.00 (dd, J=6.8, 2.2Hz, 2H), 3.77-3.86 (m, 5H), 3.66-3.77 (m, 10H), 2.77 (t, J=7.1Hz, 4H), 2.60 (t, J=5.8Hz, 2H), 2.51 (J= 7.1Hz, 4H), 1.66 (q, J=5.6Hz, 2H); HRMS [M+H]+ calculated for $C_{21}H_{37}O_9N$ 448.2541; found 448.2534.

Example Amine 6

124.8g VEEA (0.67 equivalents) and 0.23g BHT stabiliser were heated to 77°C in the same apparatus as example Amine 1. A total of 33.6ml 2-(2-aminoethoxy) ethanol (0.34 equivalents) was injected in two approximately equal aliquots, each of which caused a small exotherm. After the second exotherm had subsided the temperature was maintained at 83°C for a further 7.0 hours. 1H-NMR (500MHz, $CDCl_3$) δ 6.47 (dd, J=14.3, 6.8Hz, 2H), 4.22 (t, J=4.8Hz, 4H), 4.17 (dd, J=14.3, 2.2Hz, 2H), 4.00 (dd, J=6.8, 2.2Hz, 2H), 3.81-3.86 (m, 4H), 3.65-3.75 (m, 10H), 3.51-3.56 (m, 4H), 3.16 (s, 1H), 2.84 (t, J=7.2Hz, 4H), 2.64 (t, J=5.4Hz, 2H), 2.49 (t, J=7.2Hz, 4H); HRMS [M+H]+ calculated for $C_{22}H_{39}O_{10}N$ 478.2647; found 478.2640.

Example Amine 7

139.7g VEEA (0.75 equivalents) and 0.23g BHT stabiliser were heated to 77°C in the same apparatus as example Amine 1. A total of 16.9g solid 1,3 diamino-2-propanol (0.19 equivalents) was added in two approximately equal aliquots, each of which caused a small exotherm. After the second exotherm had subsided the temperature was maintained at 83°C for a further 7.0 hours. 1H-NMR (500MHz, $CDCl_3$) δ 6.48 (dd, J=14.3,6.8Hz, 4H), 4.23 (td, J=4.8,1.0Hz, 8H), 4.18 (dd, J=14.3,2.2Hz, 4H), 4.00 (dd, J=6.8,2.2Hz, 4H), 3.82-3.84 (m, 8H), 3.69-3.77 (m, 17H), 3.44 (s, 1H), 2.74-2.88 (m, 8H), 2.48 (t, J=7.0Hz, 8H), 2.36-2.46 (m, 4H). HRMS [M+H]+ calculated for $C_{39}H_{66}O_{17}N_2$ 835.4434; found 835.4415.

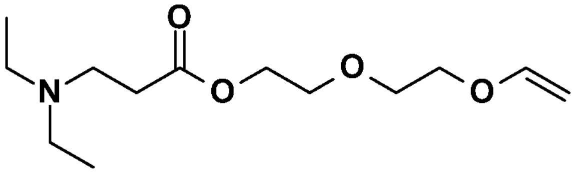
The amounts and types of the components used for the synthesis of each amine are summarised in table 1, with the volumes of the amines used now converted into grams.

Table 1 – Components for synthesis of amine functional vinyl ethers

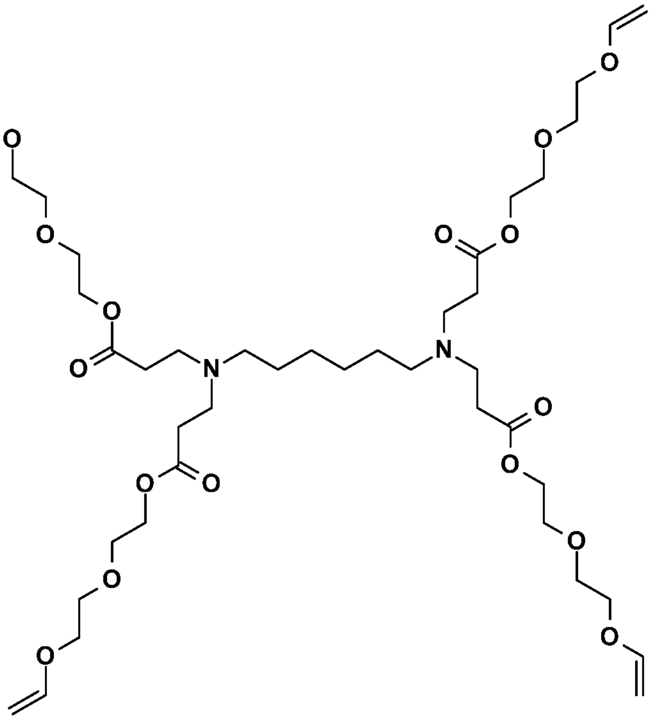
	Example Amine no.							
	Comp. 1	**1**	**2**	**3**	**4**	**5**	**6**	**7**
VEEA	111.60	121.00	111.60	124.10	148.49	130.34	124.75	139.65
BHT	0.20	0.20	0.10	0.20	0.25	0.23	0.23	0.23
Diethylamine	43.80							
Hexamethylene diamine		18.90						
Jeffamine EDR148			22.20					
DMAPAPA				35.40				
Lupasol FG					30.00			
3 amino 1 propanol						26.29		
2-(2-aminoethoxy) ethanol							35.22	
1,3 diamino 2 propanol								16.90
Total	155.6	140.1	133.9	159.7	178.74	156.86	160.2	156.78

The amounts in the table refer to grams.

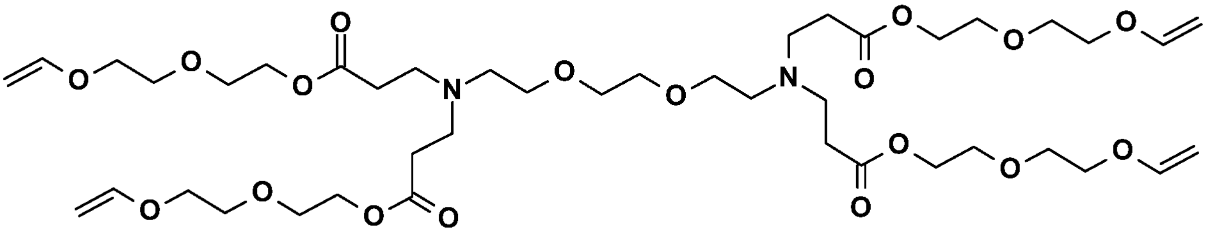
The structures of the product amines are shown below:



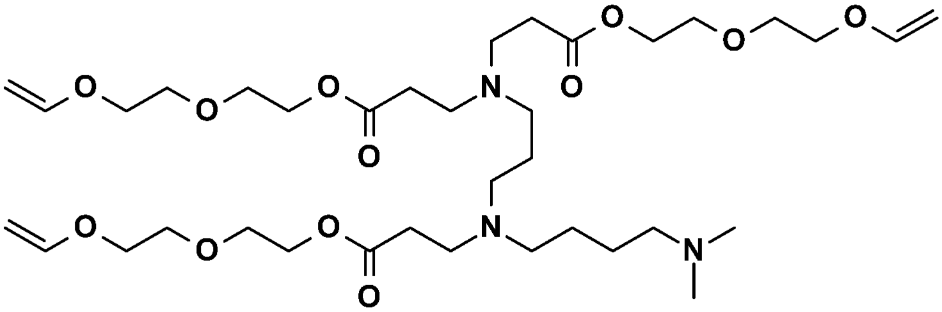
Comparative amine 1



Amine 1

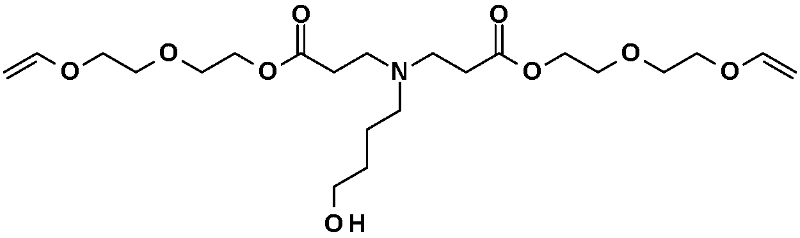


Amine 2

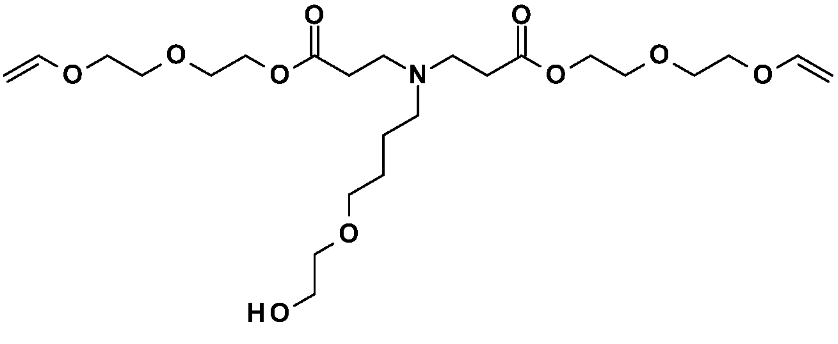


Amine 3

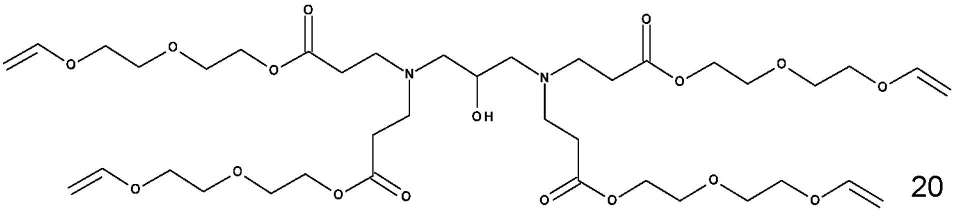
Amine 4 is a branched polyethylene imine structure with approximately 18.6 VEEA units reacted into each molecule



Amine 5



Amine 6



Amine 7

Example 2 – Ink Formulations with Magenta Pigment

Ink formulations were prepared by the following method.

First, the photoinitiator components and monomer (MPDDA) were placed in a glass jar and shaken at 200rpm on a IKA HS501 laboratory shaker. Once the photoinitiator components were dissolved and a clear solution was obtained, the stabiliser (Genorad 26) and wetting aid (TEGO Rad 2300) were added to the glass flask and shaken for a few minutes until thoroughly mixed. A pigment dispersion containing 33% Pigment Violet 19, UV diluent, dispersant and UV stabiliser was added and shaken to obtain a homogeneous composition by the same method. The amines of Example 1 were individually added to this common base to create the ink formulations for testing; the amounts and types of the components used each ink formulation are provided in table 2.

The same magenta dispersion was used in each of the example inks. The magenta dispersion was prepared using Pigment Violet 19, UV diluent, dispersant and UV stabiliser. The amount of pigment used in the dispersion was 33 % by weight.

Table 2 – Components for Magenta ink formulations

	Magenta Ink formulation no.						
Components:	**1**	**2**	**3**	**4**	**5**	**6**	**7**
MPDDA	56	56	56	56	56	56	56
Omnirad 819	4	4	4	4	4	4	4
Esacure 1001M	3	3	3	3	3	3	3
TegoRad 2300	1	1	1	1	1	1	1
Genorad 26	1	1	1	1	1	1	1
Magenta pigment dispersion	10	10	10	10	10	10	10
Amine 1	25						
Amine 2		25					
Amine 3			25				
Amine 4				25			
Amine 5					25		
Amine 6						25	
Amine 7							25
Total	100	100	100	100	100	100	100

Amines 1 to 7 are prepared as above in example 1. The amounts in the table refer to wt% based on total weight of the composition.

Comparative ink formulations containing the magenta pigment were also produced. The amounts and types of the components used each ink formulation are provided in table 3.

Table 3 – Components for Magenta comparative ink formulations

	Comparative Magenta Ink formulation no.						
Components:	**Comp 1**	**Comp 2**	**Comp 3**	**Comp 4**	**Comp 5**	**Comp 6**	**Comp 7**
MPDDA	56	56	56	56	56	56	56
Omnirad 819	4	4	4	4	4	4	4
Esacure 1001M	3	3	3	3	3	3	3
Tego Rad 2300	1	1	1	1	1	1	1
Genorad 26	1	1	1	1	1	1	1
Magenta pigment dispersion	10	10	10	10	10	10	10
MPDDA	25						
DVE-2		25					
Aminopropyl vinyl ether			25				
Comparative Amine 1				25			
CN381					25		
Ebecryl LEO10552						25	
Genomer 5275							25
Total	100	100	100	100	100	100	100

Comparative amine 1 was prepared as above in example 1. The amounts in the table refer to wt% based on total weight of the composition.

Example 3 – Magenta Ink Testing

The magenta inks and comparative inks of Example 2 were tested for viscosity, surface cure, scratch resistance, tape test and rub test using the methods outlined above in the general experimental section. The results are provided in table 4 below.

Table 4 –Magenta ink formulation Testing

Magenta Ink formulation no.							
Test	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Viscosity cP 25°C	23.04	23.42	20.49	31.62	19.42	19.75	23.58
Cure on BJ995 8µm 50m/min Hg Arc							
Surface cure	4	4	4	4.5	4	4	4
Scratch	4	4	4	4.5	3.5	4	4
ISO tape	95%	97%	97%	98%	97%	98%	98%
Magic tape	98%	99%	99%	99%	99%	99%	99%
MEK double rubs	100+	100+	100	100+	100+	100+	100+
Cure on BJ995 8µm 50m/min 395nm LED + Hg Arc							
Surface cure score (5 best)	4	4	4	4.5	4	4	4
Scratch (5 best)	4	4	5	5	4	4	4
ISO tape	95%	98%	80%	95%	95%	97%	97%
Magic tape	98%	99%	95%	99%	99%	99%	98%
MEK Double Rub	100+	100+	100+	100+	100+	100+	100+
Comparative Magenta Ink formulation no.							
Test	**Comp. 1**	**Comp. 2**	**Comp. 3**	**Comp. 4**	**Comp. 5**	**Comp. 6**	**Comp.7**
Viscosity cP 25°C	9.65	6.78	78.46	10.01	19.19	28.34	47.17
Cure on BJ995 8µm 50m/min Hg Arc							
Surface cure	2	2	2	3	4	4	4.5
Scratch	3	3	1	3	3	4	4.5
ISO tape	NA	NA	NA	20%	10%	99%	98%
Magic tape	NA	NA	NA	85%	50%	99%	99%
MEK double rubs	100+ (thins)	100+ (thins)	3	40	20	100+	100+
Cure on BJ995 8µm 50m/min 395nm LED + Hg Arc							
Surface cure score (5 best)	2	2	2	3	4	4	4.5
Scratch (5 best)	3	3	3	3	4	3.5	4.5
ISO tape	NA	NA	NA	20%	10%	99%	97%
Magic tape	NA	NA	NA	50%	70%	99%	99%
MEK Double Rub	100+ thins	100+ thins	4	90	60	100+	100+

Example 4 – Ink Formulations with Cyan Pigment

Ink formulations were prepared according to the same method as for the magenta inks outlined in Example 2. The cyan pigment dispersion contained 42.5 wt% Pigment Blue 15:4.

The amounts and types of the components used each ink formulation are provided in table 5.

Table 5 – Components for Cyan ink formulations

	Cyan Ink formulation no.						
Components:	**1**	**2**	**3**	**4**	**5**	**6**	**7**
MPDDA	73	73	73	73	73	73	73
Omnirad 819	4	4	4	4	4	4	4
Esacure 1001M	3	3	3	3	3	3	3
Tego Rad 2300	1	1	1	1	1	1	1
Cyan pigment dispersion	4	4	4	4	4	4	4
Amine 1	15						
Amine 2		15					
Amine 3			15				
Amine 4				15			
Amine 5					15		
Amine 6						15	
Amine 7							15
Total	100	100	100	100	100	100	100

Amines 1 to 7 are prepared as above in example 1. The amounts in the table refer to wt% based on total weight of the composition.

Comparative ink formulations containing the cyan pigment were also produced. The amounts and types of the components used each ink formulation are provided in table 6.

Table 6 – Components for Cyan comparative ink formulations

	Comparative Cyan Ink formulation no.						
Components:	**Comp 1**	**Comp 2**	**Comp 3**	**Comp 4**	**Comp 5**	**Comp 6**	**Comp 7**
MPDDA	73	73	73	73	73	73	73
Omnirad 819	4	4	4	4	4	4	4
Esacure 1001M	3	3	3	3	3	3	3
Tego Rad 2300	1	1	1	1	1	1	1
Cyan pigment dispersion	4	4	4	4	4	4	4
MPDDA	15						
DVE-2		15					
Aminopropyl vinyl ether			15				
Comparative Amine 1				15			
CN381					15		
Ebecryl LEO10552						15	
Genomer 5275							15
Total	100	100	100	100	100	100	100

Comparative amine 1 was prepared as above in example 1. The amounts in the table refer to wt% based on total weight of the composition.

Example 5 – Cyan Ink Testing

The cyan inks and comparative inks of Example 4 were tested for viscosity, surface cure, scratch resistance, tape test and rub test using the methods outlined above in the general experimental section. The results are provided in table 7 below.

Table 7 –Cyan ink formulation Testing

Cyan Ink formulation no.							
Test	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Viscosity cP 25°C	13.41	12.93	12.36	15.64	12.30	12.33	13.30
Cure on BJ995 8µm 50m/min Hg Arc							
Surface cure	4	4	4	4	4	4	4
Scratch	3	3	3	4	3	3	3
ISO tape	85%	90%	80%	95%	85%	92%	80%
Magic tape	98%	99%	99%	99%	99%	98%	99%
MEK double rubs	100+	100+	100+	100+	100+	100+	100+
Cure on BJ995 8µm 50m/min 395nm LED + Hg Arc							
Surface cure score (5 best)	4	4	4	4	4	4	4
Scratch (5 best)	3.5	3.5	4	4	3	4	3
ISO tape	98%	98%	90%	98%	97%	97%	98%
Magic tape	98%	99%	99%	99%	99%	98%	99%
MEK Double Rub	100+	100+	100+	100+	100+	100+	100+
Comparative Cyan Ink formulation no.							
Test	**Comp. 1**	**Comp. 2**	**Comp. 3**	**Comp. 4**	**Comp. 5**	**Comp. 6**	**Comp.7**
Viscosity cP 25°C	8.38	6.53	24.07	8.26	11.94	15.00	20.36
Cure on BJ995 8µm 50m/min Hg Arc							
Surface cure	2	2	2	4	4	3.5	4
Scratch	2	2	2	2	3	3	4
ISO tape	NA	NA	NA	30%	20%	98%	97%
Magic tape	NA	NA	NA	90%	80%	98%	98%
MEK double rubs	100+ (thins)	100+ (thins)	50	80	100+	100+ (thins)	100+
Cure on BJ995 8µm 50m/min 395nm LED + Hg Arc							
Surface cure score (5 best)	2	2	2.5	4	4	3	4
Scratch (5 best)	2	2	2	3	4	2	4
ISO tape	NA	NA	70%	50%	20%	98%	98%
Magic tape	NA	NA	97%	97%	95%	98%	99%
MEK Double Rub	100+ thins	100+ thins	100+ thins	100+	100+	100+ thins	100+

Example 6 – Nozzle Plate Wetting Ink Formulations

Ink formulations were prepared according to the same method as for the magenta inks. The black pigment dispersion contained 45 wt% Pigment Black 7.

The amounts and types of the components used each ink formulation are provided in table 8.

Table 8 –Nozzle Plate Wetting Ink formulations

	Nozzle Plate Wetting Ink formulation no.						
Components:	**1**	**2**	**3**	**4**	**5**	**6**	**7**
HDDA	75.9	75.9	75.9	75.9	75.9	75.9	75.9
Omnirad TPO	7.5	7.5	7.5	7.5	7.5	7.5	7.5
TegoRad 2300	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Carbon black dispersion	6.3	6.3	6.3	6.3	6.3	6.3	6.3
Amine 1	9.4						
Amine 2		9.4					
Amine 3			9.4				
Amine 4				9.4			
Amine 5					9.4		
Amine 6						9.4	
Amine 7							9.4
Total	100	100	100	100	100	100	100

Amines 1 to 7 are prepared as above in example 1. The amounts in the table refer to wt% based on total weight of the composition.

Comparative ink formulations containing the black pigment were also produced. The amounts and types of the components used each ink formulation are provided in table 9.

Table 9 – Components for Nozzle Plate Wetting Comparative Ink Formulations

	Nozzle Plate Wetting Comparative Ink formulation no.					
Components:	**Comp 1**	**Comp 2**	**Comp 3**	**Comp 4**	**Comp 5**	**Comp 6**
HDDA	75.9	75.9	75.9	75.9	75.9	75.9
Omnirad TPO	7.5	7.5	7.5	7.5	7.5	7.5
TegoRad 2300	0.9	0.9	0.9	0.9	0.9	0.9
Carbon black dispersion	6.3	6.3	6.3	6.3	6.3	6.3
HDDA	9.4					
DVE-2		9.4				
1,4-Butanediol divinyl ether			9.4			
Cyclohexane dimethanol divinyl ether				9.4		
Aminopropyl vinyl ether					9.4	
Comp. Amine 1						9.4
Total	100	100	100	100	100	100

Comparative Amine 1 was prepared as above in example 1. The amounts in the table refer to wt% based on total weight of the composition.

Example 7 – Nozzle Plate Wetting Testing

The nozzle plate wetting inks and comparative inks of Example 6 were tested for their effect on nozzle plate wetting using the protocol described above. The results are provided in table 10 below.

	Nozzle Plate Ink formulation no.						
Test	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Nozzle Plate Wetting	acceptable	acceptable	acceptable	acceptable	acceptable	acceptable	acceptable
	Comparative Nozzle Plate Ink formulation no.						
Test	**Comp. 1**	**Comp. 2**	**Comp. 3**	**Comp. 4**	**Comp. 5**	**Comp. 6**	
Nozzle Plate Wetting	acceptable	Not acceptable	Not acceptable	Not acceptable	acceptable	acceptable	

The nozzle plate wetting results are also shown in Figure 1. Figure 1a shows clearly that the comparative examples 2, 3 and 4 result in wetting of the nozzle plate after the immersed nozzle plate has been heated in the oven for 2 weeks. Figure 1b shows that all of the inks of the present invention do not result in wetting of the nozzle plate after the immersed nozzle plate has been heated in the oven for 2 weeks. Therefore the inks of the present invention appear to result in reduced degradation of the nozzle plate non-wetting coating.

Example 8 – Secondary Amine Functional Vinyl Ether Products

Synthesis of secondary amine functional vinyl ethers was carried out in a manner analogous to Example 1 using double the relative amount of amine to Michael acceptor. Using double the amount of amine promotes the formation of the secondary amine product. In Example 1, the amount of amine used is chosen to promote the formation of the tertiary amine product.

The amounts and components used in the synthesis of the secondary amine functional vinyl ethers are provided in Table 11.

Table 11 –Components for Synthesis of Secondary Amine Functional Vinyl Ethers

	Example Amine no.			
	8	**9**	**10**	**11**
VEEA	111.60	93.10	126.62	126.62
BHT	0.10	0.16	0.21	0.21
Jeffamine EDR148	44.40			
DMAPAPA		79.65		
3 amino 1 propanol			51.07	
1,3 diamino 2 propanol				30.64
Total	156.10	172.91	177.90	157.47

The amounts in the table refer to grams.

Example 9 – Stability of Secondary and Tertiary Amine Functional Vinyl Ethers

The secondary amines produced in Example 8 and the tertiary amines produced in Example 1 were tested for stability compared to a primary amine.

For testing, 15 parts of each amine functional vinyl ether (aminopropyl vinyl ether, and example amines 2, 3, 5, 7, 8, 9, 10, and 11) were blended with 85 parts of MPDDA.

The viscosity was measured immediately using a 50mm 1 degree cone and plate at 25°C and 100s^{-1} on an Anton Paar MCR300. The viscosity measurements were repeated after ageing the samples for 5 days and 10 days at room temperature. The results are reported in table 12.

Table 12 –Stability of Secondary and Tertiary Amine Functional Vinyl Ethers

Amine Example no	Amine used for synthesis	Type of amine	Viscosity			
			Immediate	5 days	10 days	31 days
	MPDDA (comparative)	No amine	5.2	5.4	5.2	5.4
	Aminopropyl vinyl ether (comparative)	primary	9.4	16.3	21.7	38.6
2	Jeffamine EDR148	tertiary	8.4	8.2	8.1	8.3
8	Jeffamine EDR148	secondary	9.3	10.5	10.5	11.7
3	DMAPAPA	tertiary	7.6	7.8	7.7	7.7
9	DMAPAPA	secondary	10.2	13.3	13.8	14.9
5	3 amino 1 propanol	tertiary	7.6	7.6	7.5	7.6
10	3 amino 1 propanol	secondary	8.0	10.4	10.3	10.8
7	1,3 diamino 2 propanol	tertiary	8.5	8.4	8.1	8.6
11	1,3 diamino 2 propanol	secondary	9.6	12.5	13.0	13.8

The blend of primary amine (amino propyl vinyl ether) with MPDDA is very unstable showing a big increase in viscosity over time.

The amine functional vinyl ethers synthesised in examples 1 and 8 have significantly improved stability showing small or almost no change in viscosity over time. Further, the tertiary amine functional vinyl ethers produced in Example 1 (amine 2, 3, 5 and 7) demonstrate the greatest stability over time.

Claims

1. An ink composition comprising an amine functional vinyl ether compound having at least two vinyl ether groups, and a monomer and wherein the ink composition has a viscosity of 5.0 to 70 mPa.s at 25 °C.

2. The ink composition of any one of the previous claims wherein the amine functional vinyl ether compound has at least two amine functional groups.

3. The ink composition of claim 2 wherein each of the amines in the amine functional vinyl ether compound is a secondary or tertiary amine.

4. The ink composition of claim 3 wherein each of the amines in the amine functional vinyl ether compound is a tertiary amine.

5. The ink composition of any one of the previous claims wherein the amine functional vinyl ether compound has a molecular weight of from 500 to 5,000.

6. The ink composition of claim 5 wherein the amine functional vinyl ether compound has a molecular weight of from 500 to 1,200.

7. The ink composition of any one of the previous claims wherein the amine functional vinyl ether compound has a viscosity of less than 1000 mPa.s at 25ºC.

8. The ink composition of any one of the previous claims wherein the amine functional vinyl ether compound is present at 5.0 to 30 wt % based on total weight of the ink composition.

9. The ink composition of any one of the previous claims wherein in the amine functional vinyl ether compound the amine and the at least two vinyl ether groups are joined by linking groups selected from alkyl, alkenyl, alkynyl, cycloalkyl, aminoalkyl, glycol or polyglycol groups or combinations thereof.

10. The ink composition of any one of the previous claims wherein the monomer has a polymerizable functional group selected from acrylate, methacrylate, maleate, fumarate, an acrylamide functional group or a mixture thereof.

11. The ink composition of any one of the previous claims wherein the monomer is di-functional.

12. The ink composition of any one of the previous claims wherein the monomer is present at 50 to 75 wt % based on total weight of the ink composition.

13. The ink composition of any one of the previous claims wherein the monomer has a molecular weight from 100 to 500.

14. The ink composition of any one of the previous claims wherein the monomer is an acrylate compound.

15. The ink composition of claim 14 wherein the acrylate compound is a di-functional acrylate.

16. The ink composition of claim 15 wherein the di-functional acrylate is selected from hexanediol diacrylate, 3-methyl-1,5-pentanediyl diacrylate, dipropylene glycol diacrylate, neopentyl glycol diacrylate, or propoxylated neopentyl glycol diacrylate.

17. The ink composition of claim 16 wherein the di-functional acrylate is selected from hexanediol diacrylate or 3-methyl-1,5-pentanediyl diacrylate.

18. The ink composition of any one of the previous claims further comprising a photoinitiator.

19. The ink composition of claim 18 wherein the photoinitiator is selected from α-hydroxy ketones, difunctional α-hydroxy ketones, α-amino ketones, phosphine oxides, benzophenones, ketosulphones, thioxanthones, benzil ketals, benzoylformate esters, and a mixture thereof.

20. The ink composition of claim 19 wherein the photoinitiator is selected from bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, difunctional α-hydroxy ketones, ketosulphones, polymeric thioxanthones and a mixture thereof.

21. The ink composition of claim 20 wherein the photoinitiator is a mixture of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, a difunctional α-hydroxy ketone, a polymeric thioxanthone, a ketosulphone, and ethyl phenyl(2,4,6-trimethylbenzoyl)phosphinate.

22. An ink cartridge containing the ink composition as defined in any one of claim 1 to 21.

23. A printing method comprising the steps of directing a stream of droplets of the ink composition in any one of claims 1 to 22 to a substrate and optionally curing the printed ink composition for example by treating the printed ink composition to UV radiation.

24. A substrate comprising a printed deposit produced by the method defined in claim 23.

25. A printed deposit comprising a cross-linked polymer formed from an amine functional vinyl ether compound having at least two vinyl ether groups and a monomer.

Figure 1 – Nozzle Plate Wetting Tests

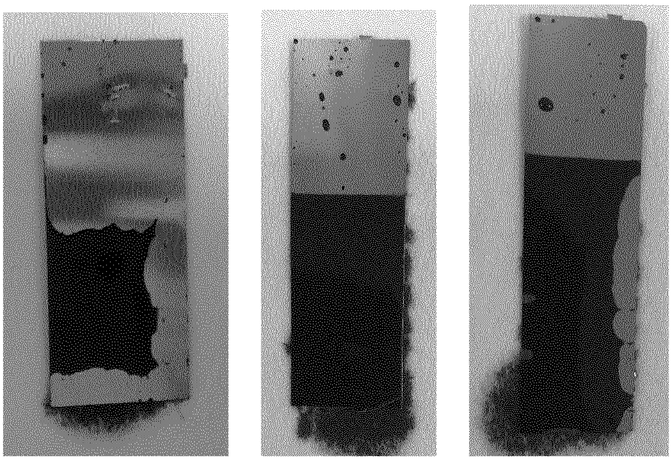


Figure 1a

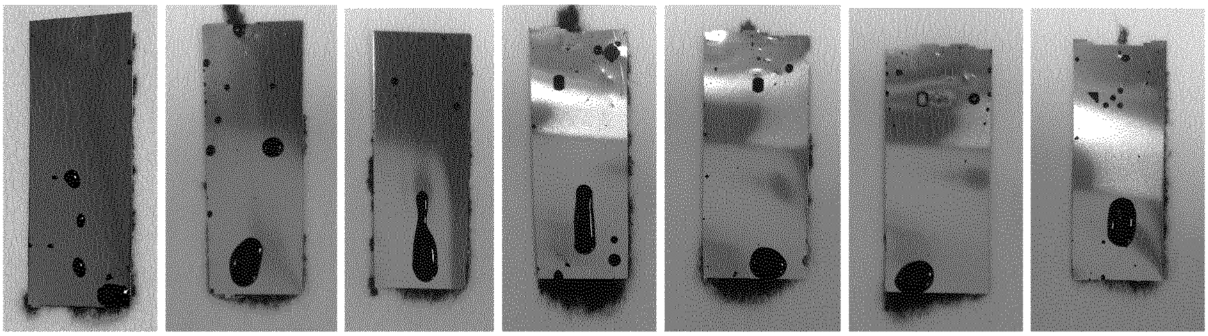


Figure 1b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/052854

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/101 C09D11/106 C09D11/38 C08F16/12
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 C08F

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	WO 2017/065957 A1 (BASF SE [DE]; BERGER SEBASTIAN [US]) 20 April 2017 (2017-04-20) claims 6, 28-29; examples -----	1-25
A	WO 2017/160784 A1 (SUN CHEMICAL CORP [US]) 21 September 2017 (2017-09-21) examples -----	1-25
A	GB 2 371 551 A (SERICOL LTD [GB]) 31 July 2002 (2002-07-31) claims; examples -----	1-25

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

☒ See patent family annex.

* Special categories of cited documents :

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"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

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"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 14 April 2021	Date of mailing of the international search report 22/04/2021
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schmitz, Volker

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/052854

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