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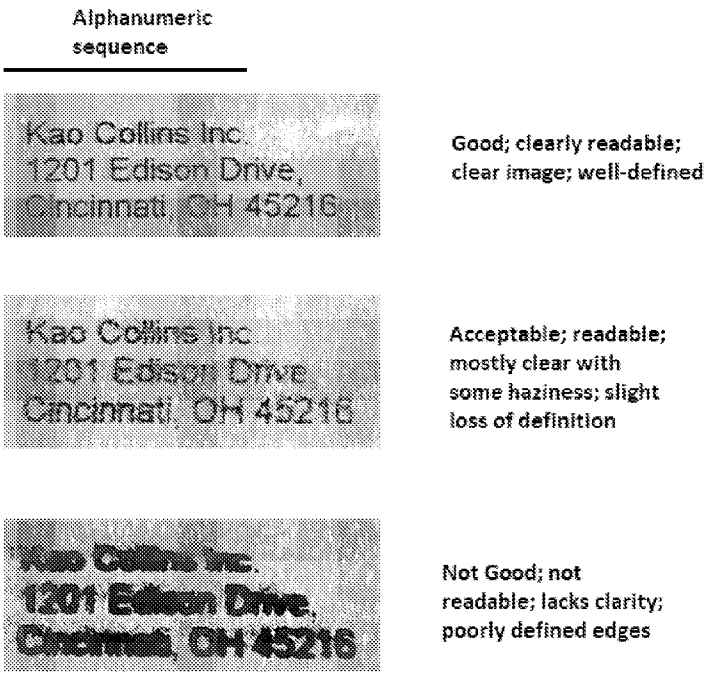
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(54) **Title:** INKJET INKS WITH LONG THROW DISTANCE



(57) **Abstract:** An inkjet ink that includes (A) a resin, which is (A1) a terpene resin or (A2) a terpene phenol resin, (B) a solvent system that includes (B1) a ketone solvent having a boiling point of less than 120 °C, and (C) a fluorosurfactant having a solubility in water at 25 °C of less than 0.1 wt. %, the inkjet ink being characterized by extended decap times, quick drying properties, and long throw distance. A printed article including the inkjet ink in dried form, and a method of forming a printed image with a thermal inkjet printhead are also provided.

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TITLE OF THE INVENTION

INKJET INKS WITH LONG THROW DISTANCE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to inkjet inks, specifically inkjet inks formulated with (A) a resin, which is (A1) a terpene resin or (A2) a terpene phenol resin, (B) a solvent system that includes (B1) a ketone solvent having a boiling point of less than 120 °C, and (C) a fluorosurfactant having a solubility in water at 25 °C of less than 0.1 wt. %.

DISCUSSION OF THE BACKGROUND

The "background" description provided herein is for the purpose of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description which may not otherwise qualify as prior art at the time of filing, are neither expressly or impliedly admitted as prior art against the present invention.

Thermal inkjet (TIJ) printing is a desirable technology for printing, coding, and marking as it offers high print resolutions at lower costs than competing technologies in the field, such as continuous inkjet (CIJ) methods. In thermal inkjet printing processes, the print cartridges contain a series of tiny chambers, each containing a heater, which produce ink droplets from thermal vaporization of an ink solvent. In the jetting process, a resistor is heated rapidly to produce a vapor bubble (hence the phrase "bubble jet"), which subsequently ejects a droplet from the orifice. This process is extremely efficient and reproducible and modern TIJ printheads for industrial graphics applications are capable of generating uniform droplets of 4 pL or smaller in volume at frequencies of 36 kHz or greater.

However, industrial marking and coding regularly requires the printing of essential information—such as personal information, codes, dating (e.g., expirations dates), and traceability information (e.g., manufacturing lot)—onto substrates having a complex surface, for example, substrates which are radial, curved, serrated, corrugated, fluted, and/or lipped. These complex substrates can introduce a large gap between the printhead and the substrate surface, which presents a significant challenge for TIJ technology that can traditionally only achieve throw distances on the order of 1 to 2 mm. When an ink must travel a distance beyond its throw distance performance capabilities before reaching the substrate surface, the resulting printed image will be of poor image quality (e.g., lack clarity, ill-defined) as a result of inaccuracies and defects in drop placement. Poor image quality is unacceptable for many applications, but particularly so for marking and coding of essential information. For this reason, even despite the other advantages, TIJ technology has had only modest acceptance in marking/coding applications because of the inability to compete with the throw distances offered by CIJ technology, which is typically in the range 5 to 12 mm.

Additionally, thermal inkjet printing can be troubled by poor reliability after periods of inactivity. For example, some inkjet inks suffer from short decap times, in which solvent losses due to prolonged exposure to air within an uncapped printhead leads to clogging/plugging of printhead nozzles, and thus unreliable ink jetting and image quality erosion over time. To improve decap performance, special solvent systems with high boiling components may be used to prevent such premature solvent losses in an uncapped printhead setting. However, these special solvent systems require extended drying times once the inks are applied, and thus inefficient overall printing processes. Therefore, it is often difficult to counterbalance the need for long decap times (the need for a slow rate of solvent loss) and short drying times (the need for a fast rate of solvent loss).

Solvent-based inkjet inks made using specific combinations of resins (such as acrylic resins and phenolic resins), solvents of varying evaporation rates, and surfactants have been reported previously to possess acceptable decap times and dry times, *see* US8778074 and US9957401—each incorporated herein by reference in its entirety. However, such systems do not report any improvements to throw distance.

SUMMARY OF THE INVENTION

In view of the forgoing, there is a need for inkjet inks that have extended decap times, dry quickly once applied, and provide long throw distance (e.g., up to 10 mm) capabilities.

Accordingly, it is one object of the present invention to provide novel inkjet inks that meet these criteria.

It is another object of the present disclosure to provide novel printed articles which contain a dried form of the inkjet inks.

It is another object of the present disclosure to provide novel methods of forming a printed image on a substrate by applying the inkjet inks onto the substrate and drying.

These and other objects, which will become apparent during the following detailed description, have been achieved by the inventors' discovery that the combination of a terpene resin or terpene phenol resin, a ketone solvent having a boiling point of less than 120 °C, and a water-insoluble fluorosurfactant, provides inkjet inks characterized by extended decap times, short drying times, and long throw distances, e.g., of up to 10 mm.

Thus, the present invention provides:

(1) An inkjet ink, comprising:

(A) a resin, which is (A1) a terpene resin or (A2) a terpene phenol resin;

(B) a solvent system comprising (B1) a ketone solvent having a boiling point of less than 120 °C; and

(C) a fluorosurfactant having a solubility in water at 25 °C of less than 0.1 wt. %.

(2) The inkjet ink of (1), wherein the resin (A) is present in an amount of 0.1 to 10 wt. %, based on a total weight of the inkjet ink.

(3) The inkjet ink of (1) or (2), wherein the resin (A) is the terpene resin (A1).

(4) The inkjet ink of (3), wherein the terpene resin (A1) is a homopolymer made from α-pinene.

(5) The inkjet ink of (1) or (2), wherein the resin (A) is the terpene phenol resin (A2).

(6) The inkjet ink of any one of (1) to (5), wherein the ketone solvent (B1) is present in an amount of 50 to 90 wt. %, based on a total weight of the inkjet ink.

(7) The inkjet ink of any one of (1) to (6), wherein a weight ratio of the ketone solvent (B1) to the resin (A) ((B1):(A)) is 10:1 to 100:1.

(8) The inkjet ink of any one of (1) to (7), wherein the ketone solvent (B1) is methyl ethyl ketone.

(9) The inkjet ink of any one of (1) to (8), wherein the solvent system (B) further comprises (B2) a glycol ether.

(10) The inkjet ink of (9), wherein the glycol ether (B2) is present in an amount of 1 to 40 wt. %, based on a total weight of the inkjet ink.

(11) The inkjet ink of any one of (1) to (10), which is substantially free of solvents having a boiling point higher than 150 °C.

(12) The inkjet ink of any one of (1) to (11), wherein the fluorosurfactant (C) is present in an amount of from 0.001 to less than 1.5 wt. %, based on a total weight of the inkjet ink.

(13) The inkjet ink of any one of (1) to (12), wherein the fluorosurfactant (C) is a partially fluorinated polymeric surfactant.

(14) The inkjet ink of any one of (1) to (13), wherein the fluorosurfactant (C) is a partially fluorinated non-ionic polymeric surfactant.

(15) The inkjet ink of any one of (1) to (14), wherein the fluorosurfactant (C) is a partially fluorinated non-ionic acrylic copolymer.

(16) The inkjet ink of any one of (1) to (15), further comprising (D) a rosin resin.

(17) The inkjet ink of (16), wherein the rosin resin (D) is present in an amount of 0.1 to 10 wt. %, based on a total weight of the inkjet ink.

(18) The inkjet ink of (16) or (17), wherein the rosin resin (D) is a hydrogenated acidic rosin.

(19) The inkjet ink of any one of (1) to (18), further comprising (E) a colorant.

(20) A printed article, comprising:

a substrate and a dried form of the inkjet ink of any one of (1) to (19) disposed on the substrate.

(21) A method of forming a printed image on a substrate, comprising:

applying the inkjet ink of any one of (1) to (19) onto the substrate with a thermal inkjet printhead; and

drying the inkjet ink.

(22) The method of (21), wherein the inkjet ink is dried by leaving exposed to air for 30 seconds or less without employing a heater.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing paragraphs have been provided by way of general introduction, and are not intended to limit the scope of the following claims. The described embodiments, together with further advantages, will be best understood by reference to the following detailed description when considered in conjunction with the accompanying drawings, wherein:

The FIGURE illustrates the throw distance evaluation for a "Good" rating (clearly readable, clear and well-defined image), an "Acceptable" rating (readable, mostly clear with

some haziness or slight loss of edge definition), and a "Not Good" rating (not readable, lacks clarity and is poorly defined) for an alphanumeric sequence.

DETAILED DESCRIPTION OF THE INVENTION

In the following description, it is understood that other embodiments may be utilized and structural and operational changes may be made without departure from the scope of the present embodiments disclosed herein.

The phrase "substantially free", unless otherwise specified, describes an amount of a particular component in the inkjet ink being less than 1 wt. %, preferably less than 0.5 wt. %, more preferably less than 0.1 wt. %, even more preferably less than 0.05 wt. %, yet even more preferably 0 wt. %, relative to a total weight of the inkjet ink.

As used herein, the terms "optional" or "optionally" means that the subsequently described event(s) can or cannot occur or the subsequently described component(s) may or may not be present (e.g., 0 wt. %).

The term "alkyl", as used herein, unless otherwise specified, refers to a straight, branched, or cyclic, aliphatic fragment having at least 1, preferably at least 2, preferably at least 3, preferably at least 4 carbon atoms, and up to 22, preferably up to 20, preferably up to 18, preferably up to 12, preferably up to 8 carbon atoms. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, isopentyl, neopentyl, hexyl, isohexyl, 3-methylpentyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, lauryl, myristyl, cetyl, stearyl, and the like, including guerbet-type alkyl groups (e.g., 2-methylpentyl, 2-ethylhexyl, 2-proylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, 2-heptylundecyl, 2-octyldodecyl, 2-nonyltridecyl, 2-decyltetradecyl, and 2-undecylpentadecyl). Cycloalkyl is a type of cyclized alkyl group. Exemplary cycloalkyl

groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, norbornyl, and adamantyl.

The term "fluoroalkyl", as used herein, unless otherwise specified, refers to an alkyl group or alkyl fragment in which one or more hydrogen atoms have been replaced by fluorine, and includes monofluoroalkyl groups (an alkyl group or alkyl fragment in which a single hydrogen has been replaced by fluorine), polyfluoroalkyl groups (an alkyl group or alkyl fragment in which more than one hydrogen has been replaced fluorine), and perfluoroalkyl groups (an alkyl group or alkyl fragment in which every hydrogen has been replaced by fluorine).

As used herein, the term "fatty" describes a compound with a long-chain (linear) hydrophobic portion made up of hydrogen and anywhere from 8 to 22 carbon atoms, which may be fully saturated or partially unsaturated.

As used herein, the term "aryl" refers to an aromatic group containing only carbon in the aromatic ring(s), such as phenyl, biphenyl, naphthyl, anthracenyl, and the like.

The term "arylalkyl", as used herein, refers to a straight, branched, or cyclic alkyl moiety (as defined above) that is substituted by an aryl group (as defined above) which may itself be optionally substituted by an alkyl group, examples of which include, but are not limited to, benzyl, phenethyl, 3-phenylpropyl, 2-phenylpropyl, 1-phenylpropyl, 4-phenylbutyl, 3-phenylbutyl, 2-phenylbutyl, 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 2,4-dimethylbenzyl, 2-(4-ethylphenyl)ethyl, 3-(3-propylphenyl)propyl, and the like.

As used herein, "ethylenically unsaturated" refers to groups containing a C=C which are curable/photopolymerizable such as (meth)acrylate, (meth)acrylamide, vinyl, allyl, and the like. The term "(meth)acrylate" is used herein to refer to both acrylate and methacrylate groups. In other words, this term should be read as through "meth" is optional. Further, the

term "(meth)acrylate" is used generally to refer to both acrylic acid-based compounds and acrylic ester-based compounds. Similarly, the term "(meth)acrylamide" " is used herein to refer to both acrylamide and methacrylamide groups.

Unless otherwise specified, "water-soluble" refers to compounds/components having a solubility in water at 25 °C of greater than or equal to 0.1 wt. % (≥ 1 g per L of water), including compounds/components which are freely soluble/miscible in water. While "water-insoluble" refers to compounds/components having a solubility in water at 25 °C of less than 0.1 wt. % (< 1 g per L of water).

Throughout the specification, the term "boiling point" (b.p.) refers to the boiling point of a liquid measured at sea-level atmospheric pressure (i.e., 760 mmHg or 1 atmosphere), also called the normal boiling point, unless specified otherwise.

The term "decap behavior" herein, means the ability of the inkjet ink to readily eject from the printhead, upon prolonged exposure to air. The inkjet ink "decap time" is measured as the amount of time that an inkjet printhead may be left uncapped before the printer nozzles no longer fire properly, potentially because of clogging or plugging when printing resumes. Generally, nozzle(s) may become clogged (i.e., impeded, slowed) or plugged (i.e., obstructed, substantially or completely closed) by a viscous plug that forms in the nozzle(s) as a result of solvent loss, crusting of the ink, and/or kogation of various ink components in and/or around any of the nozzles. If a nozzle has become clogged, ink droplets ejected through the nozzle's orifice may be misdirected, which may adversely affect print quality. When an orifice is plugged, it becomes substantially or completely blocked. As a result of the nozzle being plugged, the ink droplets may not pass through the affected nozzle. Thus, the criteria for measuring failure to fire by a nozzle is a misdirection of ink through the nozzle's orifice to a lesser or greater degree, or a complete blockage, which can be measured by visually inspecting a printed image.

As used herein, the term "throw distance" is defined as the distance between the printhead and the surface of the substrate that can be used whilst still achieving required printed image quality.

Inkjet inks

The present disclosure is directed to inkjet inks that possess suitable physical and chemical stability at both ambient temperatures and printhead operating temperatures, are jetted reliably, and have prolonged decap times while still drying quickly after being applied onto a substrate (e.g., dry times of 30 seconds or less). Further, the combination of ingredients disclosed herein has been unexpectedly found to enable thermal inkjet printing at long throw distances, e.g., up to 10 mm.

Inkjet inks of the present disclosure generally include the following components: (A) a resin, which is (A1) a terpene resin or (A2) a terpene phenol resin, (B) a solvent system comprising (B1) a ketone solvent having a boiling point of less than 120 °C, and (C) a fluorosurfactant having a solubility in water at 25 °C of less than 0.1 wt. %.

The inkjet inks of the present disclosure may also optionally include one or more of (B2) a glycol ether as part of the solvent system (B), (D) a rosin resin, (E) a colorant, and (F) an additive.

(A) Resin

Inkjet inks of the present disclosure are formulated with a resin (A), which has been found to provide superior dry times and decap times when used in combination with a ketone solvent (B1) having a boiling point of less than 120 °C, and a water-insoluble fluorosurfactant (C).

The resin (A) may be present in the inkjet inks in an amount of at least 0.1 wt. %, preferably at least 0.2 wt. %, preferably at least 0.4 wt. %, preferably at least 0.6 wt. %, more preferably at least 0.8 wt. %, even more preferably at least 0.9 wt. %, yet even more preferably at least 1 wt. %, and up to 10 wt. %, preferably up to 9 wt. %, preferably up to 8 wt. %, preferably up to 7 wt. %, preferably up to 6 wt. %, preferably up to 5 wt. %, more preferably up to 4 wt. %, even more preferably up to 3 wt. %, yet even more preferably up to 2 wt. %, based on a total weight of the inkjet ink.

The inkjet inks may be formulated with one, or a mixture of resins (A). The one or more resins (A) employed herein are polymeric materials, either homopolymers or copolymers, that contain constitutional units derived from terpene. The resin(s) (A) employed herein may be a terpene resin (A1) and/or terpene phenol resin (A2).

<Terpene resin (A1)>

The terpene resin (A1) of the present disclosure refers to oligomers or polymers having at least 95 wt. %, preferably at least 96 wt. %, more preferably at least 97 wt. %, more preferably at least 98 wt. %, more preferably at least 99 wt. %, even more preferably at least 99.5 wt. %, yet even more preferably 100 wt. % of constitutional units derived from a polymerizable terpene(s), based on the total constitutional units (100 wt. %) of the terpene resin (A1). Terpenes have a basic skeleton $(C_5H_8)_p$ where p is a positive integer that delineates the number of isoprene units that are successively bound head to tail. For example, hemiterpenes (p = 1) have a C_5H_8 skeleton, monoterpenes (p = 2) have a $C_{10}H_{16}$ skeleton, sesquiterpenes (p = 3) have a $C_{15}H_{24}$ skeleton, and so forth.

In some embodiments, the terpene resin (A1) is based on monoterpene monomer units. The monoterpene may be a linear monoterpene (e.g., myrcene, ocimene, etc.), a monocyclic monoterpenes (e.g., limonene, γ-terpinene, α-phellandrene, β-phellandrene,

terpinolene, etc.), or a bicyclic monoterpene (e.g., 3-carene, α-pinene, β-pinene, α-fenchene, camphene, etc.), including the various stereoisomers thereof, as well as mixtures thereof. In some embodiments, the monoterpene is a monocyclic monoterpene, with particular preference to limonene. In preferred embodiments, the monoterpene is a bicyclic monoterpene, with particular preference to 3-carene, α-pinene, β-pinene, and camphene, more preferably α-pinene and/or β-pinene, even more preferably α-pinene.

Preferred inkjet inks are those formulated with a terpene resins (A1) made from polymerization or oligomerization of α-pinene. As known by those of ordinary skill in the art, such terpene resins may be readily obtained for example through catalytic polymerization/oligomerization (in solution) of α-pinene monomers, which are in turn typically derived from fractional distillation of gum and sulfate turpentines obtained from pines such as *Pistacia terebinthus*, *Pinus pinaster*, *Pinus halepensis*, *Pinus massoniana*, *Pinus merkusii*, *Pinus palustris*, *Pinus taeda*, and *Pinus ponderosa*.

In preferred embodiments, the terpene resin (A1) is a homopolymer made from α-pinene, with an α-pinene content (constitutional units derived from α-pinene) of at least 95 wt. %, preferably at least 96 wt. %, preferably at least 97 wt. %, preferably at least 98 wt. %, preferably at least 99 wt. %, more preferably at least 99.5 wt. %, even more preferably at least 99.9 wt. %, yet even more preferably 100 wt. %, based on the total constitutional units (100 wt. %) of the terpene resin (A1). While the terpene resins (A1) of the present disclosure may include small amounts of other constitutional units other than constitutional units derived from α-terpene monomers, the amount of other (e.g., non-terpene based) constitutional units is preferably less than 5 wt. %, preferably less than 3 wt. %, preferably less than 1 wt. %, more preferably less than 0.5 wt. %, even more preferably less than 0.1 wt. %, yet even more preferably 0 wt. %, based on the total constitutional units (100 wt. %) of the terpene resins (A1).

In some embodiments, the terpene resin (A1) is a homopolymer made from β-pinene, with a β-pinene content (constitutional units derived from β-pinene) of at least 95 wt. %, preferably at least 96 wt. %, preferably at least 97 wt. %, preferably at least 98 wt. %, preferably at least 99 wt. %, more preferably at least 99.5 wt. %, even more preferably at least 99.9 wt. %, yet even more preferably 100 wt. %, based on the total constitutional units (100 wt. %) of the terpene resin (A1).While the terpene resins (A1) of the present disclosure may include small amounts of other constitutional units other than constitutional units derived from β-terpene monomers, the amount of other (e.g., non-terpene based) constitutional units is preferably less than 5 wt. %, preferably less than 3 wt. %, preferably less than 1 wt. %, more preferably less than 0.5 wt. %, even more preferably less than 0.1 wt. %, yet even more preferably 0 wt. %, based on the total constitutional units (100 wt. %) of the terpene resins (A1).

Both polymeric and oligomeric forms of the terpene resin (A1) may be used herein, including combinations thereof. Typically, terpene resins (A1) are used herein that have a number average molecular weight (M_n) of at least 330 g/mol, preferably at least 340 g/mol, preferably at least 400 g/mol, preferably at least 450 g/mol, preferably at least 500 g/mol, preferably at least 550 g/mol, more preferably at least 600 g/mol, more preferably at least 650 g/mol, even more preferably at least 700 g/mol, yet even more preferably at least 750 g/mol, and up to 1,500 g/mol, preferably up to 1,300 g/mol, more preferably up to 1,100 g/mol, more preferably up to 1,000 g/mol, more preferably up to 900 g/mol, even more preferably up to 800 g/mol, yet even more preferably up to 790 g/mol.

The terpene resins (A1) may be in the form of a solid or a liquid at room temperature. When in the form of a solid, the terpene resin (A1) utilized herein may be categorized based upon its softening point (SP), for example according to a ring-and-ball softening point method. The ring-and-ball softening point is defined as the temperature at which a disk of the

sample held within a horizontal ring is forced downward a distance of 1 in. (25.4 mm) under the weight of a steel ball as the sample is heated at a prescribed rate in a glycerol bath. For example, the ring-and-ball softening point may be determined according to JIS B7410—which is incorporated herein by reference in its entirety—Measuring apparatus: Automatic Ring-and-Ball Softening Point; Tester: ASP-MGK2, manufactured by MEITECH Company Ltd.; Heating rate: 5°C/min; Temperature at which heating is started: 40°C; Measurement solvent: glycerol. In some embodiments, the terpene resin (A1) has a softening point of at least 20 °C, preferably at least 40 °C, preferably at least 60 °C, preferably at least 80 °C, more preferably at least 100 °C, more preferably at least 110 °C, more preferably at least 115 °C, more preferably at least 120 °C, even more preferably at least 125 °C, yet even more preferably at least 130 °C, and up to 160 °C, preferably up to 155 °C, preferably up to 150 °C, preferably up to 145 °C, more preferably up to 140 °C, even more preferably up to 138 °C, yet even more preferably up to 135 °C.

Bromine number is the amount of bromine (Br_2) in grams absorbed by 100 grams of a sample, and is an indicator of the degree of unsaturation of the sample. In some embodiments, the terpene resin (A1) employed in the inkjet inks has a bromine number of at least 12, preferably at least 15, preferably at least 19, preferably at least 22, more preferably at least 25, even more preferably at least 26, yet even more preferably at least 27, and up to 35, preferably up to 34, more preferably up to 33, more preferably up to 32, even more preferably up to 31, yet even more preferably up to 30, although terpene resins (A1) having a bromine number above or below (e.g., hydrogenated terpene resins (A1)) these values may also find use in the disclosed inkjet inks.

The inkjet inks of the present disclosure may be formulated with a single type of terpene resin (A1), or with a combination of two or more types of terpene resins (A1). Examples of terpene resins (A1) that may be employed in the inkjet inks herein, either alone

or in combination, include, but are not limited to, PICCOLYTE A115 (ring-and-ball SP = 112-118 °C, bromine number = 31.5), PICCOLYTE A125 (ring-and-ball SP = 122-128 °C, bromine number = 31.5), PICCOLYTE A135 (ring-and-ball SP = 132-138 °C, bromine number = 27), PICCOLYTE A135 PLUS (ring-and-ball SP = 132-138 °C), PICCOLYTE AO PLUS (oligomer, liquid), and PINOVA RESIN 2495 (ring-and-ball SP = 132-138 °C, bromine number = 27), each being made from high purity α-pinene, available from Pinova, as well as PICCOLYTE S25 (made from high purity β-pinene, ring-and-ball SP = 22-28 °C, bromine number 19), available from Pinova.

<Terpene phenol resin (A2)>

Terpene phenol resins (A2) are the copolymeric reaction products from alkylation of one or more phenolic compounds with one or more terpenes. As known by those of ordinary skill in the art, such resins may be readily obtained through copolymerization of a phenolic compound and a terpene monomer under the catalytic action of strong acids, metal salts having a condensing effect, bleaching earths, Friedel-Craft catalysts or strong Lewis acids, (e.g., boron trifluoride), and the like.

While the terpene phenol resins (A2) of the present disclosure may include small amounts of other constitutional units other than the constitutional units derived from phenolic compounds and constitutional units derived from terpene, the amount of other (e.g., non-phenol and non-terpene based) constitutional units is preferably less than 5 wt. %, preferably less than 4 wt. %, preferably less than 3 wt. %, preferably less than 2 wt. %, more preferably less than 1 wt. %, even more preferably less than 0.5 wt. %, yet even more preferably 0 wt. %, based on the total constitutional units (100 wt. %) of the terpene phenol resin (A2).

The terpene phenol resins (A2) utilized herein may be formed using any terpene having at least one olefinic double bond that is capable of being alkylated by a phenolic compound. In some embodiments, the terpene phenol resin (A2) is formed using monoterpene monomer units. The monoterpene may be a linear monoterpene (e.g., myrcene, ocimene, etc.), a monocyclic monoterpenes (e.g., limonene, γ-terpinene, α-phellandrene, β-phellandrene, terpinolene, etc.), or a bicyclic monoterpene (e.g., 3-carene, α-pinene, β-pinene, α-fenchene, camphene, etc.), including the various stereoisomers thereof, as well as mixtures thereof. In some embodiments, the monoterpene is a monocyclic monoterpene, with particular preference to limonene. In preferred embodiments, the monoterpene is a bicyclic monoterpene, with particular preference to 3-carene, α-pinene, β-pinene, and camphene, more preferably α-pinene and/or β-pinene.

A phenolic compound has at least one hydroxyl group directly bonded to a phenyl ring. All mono- or polyvalent phenolic compounds are useful in the preparation of the terpene phenol resin (A2) described herein provided that the phenolic compound has at least two replaceable hydrogen atoms in ortho- and/or para-positions with respect to at least one hydroxyl group. That is, the phenolic compound should be capable of being polyalkylated (e.g., bis-alkylated) with the terpene(s), and thus should have at least two available ortho-/para-positions with respect to at least one hydroxyl group for alkylation.

In preferred embodiments, the phenolic compound is phenol, which is considered the parent unsubstituted phenolic compound (i.e., contains one hydroxyl group bonded directly to the phenyl ring with no other substitution). Alternatively, the phenolic compound may be substituted at up to three positions in addition to the phenolic hydroxyl group, wherein one, two or three of the aromatic hydrogens of phenol are replaced with an equal number of substituents, each independently selected from a hydroxyl group; a C_1-C_{22} alkyl group, preferably a C_2-C_{18} alkyl group, more preferably a C_3-C_{12} alkyl group, even more preferably

a C_4-C_9 alkyl group, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl; a C_1-C_{22} alkoxy group, preferably a C_2-C_{12} alkoxy group, more preferably a C_3-C_6 alkoxy group, for example, methoxy, ethoxy, and isopropoxy; an aryl group; an arylalkyl group, for example a benzyl group; and a halo group such as chlorine, bromine, fluorine and iodine.

Specific examples of substituted phenolic compounds include, but are not limited to, o-cresol, m-cresol, p-cresol, 2,5-xylenol, 2,3-xylenol, 3,4-xylenol, 3,5-xylenol, 2,3,5-trimethylphenol, isopropylphenol (e.g., 4-isopropylphenol), tert-butylphenol (e.g., 4-tert-butylphenol), amylphenol (e.g., 4-tert-amylphenol), heptylphenol (e.g., 4-heptylphenol), octylphenol (e.g., o-octylphenol, p-octylphenol, etc.), nonylphenol (e.g., 4-(2,4-dimethylheptan-3-yl)phenol), decylphenol, dodecylphenol, bisphenols such as diphenylolpropane (bisphenol-A), phenylphenol (e.g., 3-phenylphenol), cumylphenol, mequinol, benzyloxyphenol, guaiacol, ethoxyphenol (e.g., 4-ethoxyphenol), as well as polyhydric phenolic compounds such as resorcinol, pyrogallol, catechol, and p-hydroquinone, including mixtures of two or more of any of the above. Also included are fused ring phenols such as naphthols (e.g., 1-naphthol, 2-naphthol, etc.) and similar compounds.

In preferred embodiments, the terpene phenol resin (A2) employed in the inkjet ink is a copolymer formed from phenol and one or more of α-pinene, β-pinene, and limonene.

The molecular weight of the terpene phenol resin (A2) may vary depending on the monomers utilized, the reaction conditions, among many other factors, but typically terpene phenol resins (A2) are used that have a weight average molecular weight (Mw) of at least 400 g/mol, preferably at least 500 g/mol, more preferably at least 600 g/mol, even more preferably at least 700 g/mol, and up to 3,000 g/mol, preferably up to 2,500 g/mol, more preferably up to 2,000 g/mol, even more preferably up to 1,500 g/mol, yet even more preferably up to 1,000 g/mol.

The terpene phenol resin (A2) utilized herein may be categorized based upon its softening point (SP), for example according to the ring-and-ball softening point method as described heretofore (e.g., according to JIS B7410—incorporated herein by reference in its entirety). In some embodiments, the terpene phenol resin (A2) has a softening point of at least 60 °C, preferably at least 80 °C, preferably at least 90 °C, preferably at least 100 °C preferably at least 105 °C, more preferably at least 110 °C, even more preferably at least 115 °C, yet even more preferably at least 120 °C, and up to 160 °C, preferably up to 155 °C, preferably up to 150 °C, preferably up to 145 °C, preferably up to 140 °C, more preferably up to 135 °C, even more preferably up to 130 °C, yet even more preferably up to 125 °C.

The hydroxyl value (OHV) is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid taken up on acetylation of one gram of a chemical substance that contains free hydroxyl groups. Therefore, the hydroxyl value, or the measure of the relative hydroxyl content of the terpene phenol resin (A2), is directly correlated to the content of the phenolic compound(s) within the terpene phenol resin (A2), with higher hydroxyl values indicating higher phenolic compound incorporation into the copolymer (and lower terpene incorporation). Hydroxyl values can be determined according to Japanese Industrial Standards JIS K 0070: 1992 "Test methods for acid value, saponification value, ester value, iodine value, hydroxyl value, and unsaponifiable matter of chemical products."

The hydroxyl value of the terpene phenol resin (A2) employed in the disclosed inkjet inks may vary, for example, from 10 mgKOH/g to 150 mgKOH/g. However, in terms of decap behavior and running stability, preferred terpene phenol resins (A2) are those having a hydroxyl value of at least 10 mgKOH/g, preferably at least 15 mgKOH/g, preferably at least 20 mgKOH/g, preferably at least 22 mgKOH/g, preferably at least 24 mgKOH/g, preferably at least 25 mgKOH/g, preferably at least 28 mgKOH/g, preferably at least 30 mgKOH/g,

preferably at least 32 mgKOH/g, preferably at least 34 mgKOH/g, more preferably at least 36 mgKOH/g, even more preferably at least 38 mgKOH/g, yet even more preferably at least 40 mgKOH/g, and up to 80 mgKOH/g, preferably up to 75 mgKOH/g, preferably up to 70 mgKOH/g, preferably up to 65 mgKOH/g, preferably up to 60 mgKOH/g, more preferably up to 55 mgKOH/g, even more preferably up to 50 mgKOH/g, yet even more preferably up to 45 mgKOH/g, with hydroxyl values (OHV) of 20 to 60 mgKOH/g being the most preferred.

Examples of suitable terpene phenol resins (A2) that may be employed in the inkjet inks herein, either alone or in combination, include, but are not limited to, YS POLYSTER products such as YS POLYSTER U130 (OHV = 25 mgKOH/g; SP = 130 °C), YS POLYSTER U115 (OHV = 30 mgKOH/g; SP = 115 °C), YS POLYSTER T160 (OHV = 60 mgKOH/g; SP = 160 °C), and YS POLYSTER T145 (OHV = 65 mgKOH/g; SP = 145 °C), available from Yasuhara Chemical Co. Ltd., and DERTOPHENE products such as DERTOPHENE T (OHV = 20-50 mgKOH/g; SP = 95 °C; Mw = 700 g/mol), DERTOPHENE T105 (OHV = 40 mgKOH/g; SP = 105 °C; Mw = 700 g/mol), DERTOPHENE T115 (OHV = 50 mgKOH/g; SP = 120 °C; Mw = 700 g/mol), and DERTOPHENE T160 (OHV = 60 mgKOH/g; SP = 160 °C; Mw = about 1,000 g/mol), available from DRT/Pinova. A particularly preferred terpene phenol resin (A2) is YS POLYSTER U115.

(B) Solvent System

In many printing processes that utilize solvent-based inks, and particularly in thermal inkjet printing, the selection of an appropriate solvent system may impact the reliability of the printing process, the properties/appearance of the printed ink product, and the overall printing process efficiency. For example in thermal inkjet printing, the choice of solvent system may 1) aid bubble formation during the jetting process resulting in reliable ink jetting, 2) affect the

stability/volatility of the inkjet inks by changing the interaction dynamics between the solvent(s) and the various inkjet ink components and thus the decap behavior, kogation, and/or drop trajectory, 3) impact the adhesion, rub and scratch resistance, and optical density properties of the printed image through the interactive forces between the solvent system and the other inkjet ink components even though the solvent(s) may no longer be present, or may be present in lesser amounts, after drying, and/or 4) influence the drying time after application or the equipment needed to dry the applied ink.

In light of the above, particular preference is given herein to inkjet inks with a solvent system (B) that includes one or more (B1) ketone solvent(s). The inclusion of the ketone solvent (B1) may aid solvation of the inkjet ink components and provide the inkjet inks with acceptable volatility for the purposes of dry times. It is preferred that the ketone solvent (B1) constitutes a majority of the solvent system (B) used in the inkjet inks herein, i.e., that the ketone solvent (B1) constitutes at least 50 wt. %, preferably at least 60 wt. %, preferably at least 70 wt. %, more preferably at least 80 wt. %, even more preferably at least 85 wt. %, yet even more preferably at least 90 wt. %, and up to 100 wt. %, preferably up to 98 wt. %, more preferably up to 96 wt. %, even more preferably up to 94 wt. %, yet even more preferably up to 92 wt. %, based on a total weight of the solvent system (B). In some embodiments, the ketone solvent (B1) is present in the inkjet inks in an amount of at least 50 wt. %, preferably at least 55 wt. %, more preferably at least 60 wt. %, more preferably at least 64 wt. %, even more preferably at least 68 wt. %, yet even more preferably at least 70 wt. %, and up to 90 wt. %, preferably up to 85 wt. %, preferably up to 82 wt. %, preferably up to 80 wt. %, more preferably up to 78 wt. %, more preferably up to 76 wt. %, even more preferably up to 74 wt. %, yet even more preferably up to 73 wt. %, based on a total weight of the inkjet ink.

In some embodiments, a weight ratio of the ketone solvent (B1) to the resin (A) ((B1):(A)) is at least 10:1, preferably at least 20:1, preferably at least 30:1, preferably at least

40:1, preferably at least 50:1, preferably at least 55:1, more preferably at least 60:1, even more preferably at least 65:1, yet even more preferably at least 70:1, and up to 100:1, preferably up to 95:1, preferably up to 90:1, more preferably up to 85:1, even more preferably up to 80:1, yet even more preferably up to 75:1.

Preferred ketone solvents (B1) are those which have a boiling point of less than 120 °C, preferably less than 115 °C, preferably less than 110 °C, preferably less than 105 °C, preferably less than 100 °C, preferably less than 95 °C, preferably less than 90 °C, preferably less than 85 °C, preferably less than 80 °C. When a ketone solvent (B1) is used which has a boiling point not greater than the above upper limit, extremely fast drying times and advantageous decap times may be realized.

The ketone solvent (B1) may contain 3, 4, 5, or 6 carbon atoms. Examples of ketone solvents, which may be used singly or in combination in the disclosed inkjet inks, include, but are not limited to, acetone, methyl ethyl ketone (MEK), 3-pentanone, methyl n-propyl ketone, methyl isopropyl ketone, ethyl isopropyl ketone, and methyl isobutyl ketone. In particular, extremely fast drying times and advantageous decap times may be realized when the solvent system (B) includes methyl ethyl ketone.

The solvent system (B) may also optionally include a glycol ether (B2) to further improve decap performance without substantially worsening ink dry times. The glycol ether (B2) may be a monoalkyl ether, a dialkyl ether, a monoalkyl monoester ether, or a combination thereof. In preferred embodiments, the glycol ether (B2) is a monoalkyl ether, i.e., contains one free hydroxyl group. The glycol ether (B2) may contain at least 3 carbon atoms, preferably at least 4 carbon atoms, more preferably at least 5 carbon atoms, even more preferably at least 6 carbon atoms, and up to 12 carbon atoms, preferably up to 10 carbon atoms, more preferably up to 8 carbon atoms.

In some embodiments, the solvent system (B) may be formulated with a mixture of glycol ethers (B2), for example, a first glycol ether and a second glycol ether in a weight ratio of at least 1:5, preferably at least 1:4, more preferably at least 1:3, even more preferably at least 1:2, yet even more preferably at least 1:1, and up to 5:1, preferably up to 4:1, more preferably up to 3:1, even more preferably up to 2:1.

Acceptable examples of glycol ethers (B2) that may be optionally included in the disclosed inkjet inks include, but are not limited to, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-isopropyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-t-butyl ether, ethylene glycol monobutyl ether, ethylene glycol mono-isobutyl ether, diethylene glycol monomethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-isopropyl ether, propylene glycol mono-n-butyl ether, dipropylene glycol monomethyl ether, propylene glycol methyl ether acetate, ethylene glycol dimethylether, diethylene glycol dimethylether, diethylene glycol methyl ethyl ether, diethylene glycol diethylether, dipropylene glycol dimethyl ether, dipropylene glycol mono-n-propyl ether, as well as mixtures thereof.

In terms of improving decap performance of the inkjet inks without considerably lengthening ink dry times, preferred glycol ethers (B2) are those which have a boiling point of less than 214 °C, preferably less than 200 °C, preferably less than 190 °C, preferably less than 180 °C, more preferably less than 175 °C, more preferably less than 170 °C, more preferably less than 165 °C, more preferably less than 160 °C, even more preferably less than 155 °C, yet even more preferably less than 150 °C.

In light of the above, preference is given to ethylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol mono-n-propyl ether, and propylene glycol mono-n-propyl ether. In preferred embodiments, a mixture of propylene glycol ethers

is used, with specific mention being made to a mixture of propylene glycol monomethyl ether and propylene glycol mono-n-propyl ether, e.g., in a weight ratio of at least 1:5, preferably at least 1:4, more preferably at least 1:3, even more preferably at least 1:2, yet even more preferably at least 1:1, and up to 5:1, preferably up to 4:1, more preferably up to 3:1, even more preferably up to 2:1.

When employed, the glycol ether (B2) may be present in the inkjet inks in an amount of at least 1 wt. %, preferably at least 2 wt. %, more preferably at least 3 wt. %, even more preferably at least 4 wt. %, yet even more preferably at least 5 wt. %, and up to 40 wt. %, preferably up to 30 wt. %, more preferably up to 20 wt. %, even more preferably up to 15 wt. %, yet even more preferably up to 10 wt. %, based on a total weight of the inkjet ink. In some embodiments, the weight ratio of the ketone solvent (B1) to the glycol ether (B2) can be adjusted for desired drying times and decap times, typically within a range of at least 3:1, preferably at least 4:1, more preferably at least 5:1, even more preferably at least 6:1, yet even more preferably at least 7:1, and up to 30:1, preferably up to 20:1, more preferably up to 15:1, even more preferably up to 10:1, yet even more preferably up to 8:1.

In addition to the ketone solvent(s) (B1) and optionally glycol ether(s) (B2), other organic solvents which may be optionally utilized as part of the solvent system (B) herein include, but are not limited to:

- lower alcohols containing from 1 to 8 carbon atoms, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol;
- ethers (non-glycol ethers), for example ethers containing 4 to 8 carbon atoms such as diethyl ether, dipropyl ether, methyl tert-butyl ether, dibutyl ether, dioxane, and tetrahydrofuran;
- esters, including those having 3 to 8 carbon atoms, for example methyl acetate, ethyl acetate, n-butyl acetate, methyl lactate, ethyl lactate;

- alkanes, for example pentane, hexane, heptane;
- and the like, as well as mixtures of two or more thereof.

When present, the additional organic solvents may be included in amounts of up to 20 wt. %, preferably up to 15 wt. %, preferably up to 10 wt. %, preferably up to 5 wt. %, more preferably up to 4 wt. %, even more preferably up to 2 wt. %, yet even more preferably up to 1 wt. %, based on a total weight of the inkjet inks.

In preferred embodiments, the inkjet inks are substantially free of solvents having a boiling point higher than 175 °C, preferably solvents having a boiling point higher than 170 °C, preferably solvents having a boiling point higher than 165 °C, more preferably solvents having a boiling point higher than 160 °C, even more preferably solvents having a boiling point higher than 155 °C, yet even more preferably solvents having a boiling point higher than 150 °C. In preferred embodiments, the inkjet inks are substantially free of ketone solvents having a boiling point of 120 °C or greater, examples of which include but are not limited to, 3-hexanone, methyl n-butyl ketone, and cyclohexanone. In some embodiments, the inkjet inks are substantially free of lower alcohol solvents (having 1 to 8 carbon atoms). In some embodiments, the inkjet inks are substantially free of ether solvents (other than glycol ethers (B2)). In some embodiments, the inkjet inks are substantially free of glycol ethers (B2). In some embodiments, the inkjet inks are substantially free of ester solvents. In some embodiments, the inkjet inks are substantially free of additional organic solvents, that is, organic solvents other than ketone solvents (B1) and glycol ethers (B2). In preferred embodiments, the solvent system (B) consists of the ketone solvent (B1) and the glycol ether (B2).

In preferred embodiments, the inkjet inks of the present disclosure are substantially non-aqueous, meaning that no water is added to the inkjet inks other than what may be incidental amounts of moisture derived from ambient conditions. In such cases, the inkjet

inks may have less than 1 wt. %, preferably less than 0.5 wt. %, preferably less than 0.1 wt. %, more preferably less than 0.05 wt. %, even more preferably less than 0.01 wt. % of water, yet even more preferably 0 wt. %, based on the total weight of inkjet inks.

Fluorosurfactant (C)

The inkjet inks of the present disclosure are formulated with a fluorosurfactant (C). The fluorosurfactant (C) may be present in the inkjet inks in an amount of from 0.001 to less than 1.5 wt. %, for example, from at least 0.001 wt. %, preferably at least 0.005 wt. %, preferably at least 0.01 wt. %, preferably at least 0.015 wt. %, preferably at least 0.02 wt. %, preferably at least 0.04 wt. %, preferably at least 0.06 wt. %, preferably at least 0.08 wt. %, preferably at least 0.1 wt. %, preferably at least 0.12 wt. %, preferably at least 0.14 wt. %, preferably at least 0.16 wt. %, preferably at least 0.18 wt. %, more preferably at least 0.2 wt. %, even more preferably at least 0.22 wt. %, yet even more preferably at least 0.25 wt. %, and up to 1.4 wt. %, preferably up to 1.2 wt. %, preferably up to 1 wt. %, preferably up to 0.8 wt. %, more preferably up to 0.6 wt. %, even more preferably up to 0.4 wt. %, yet even more preferably up to 0.3 wt. %, based on a total weight of the inkjet ink.

Suitable fluorosurfactants (C) are those which are water-insoluble, i.e., have a solubility in water at 25 °C of less than 0.1 wt. %, preferably less than 0.09 wt. %, preferably less than 0.08 wt. %, preferably less than 0.07 wt. %, preferably less than 0.06 wt. %, preferably less than 0.05 wt. %, preferably less than 0.04 wt. %, more preferably less than 0.03 wt. %, even more preferably less than 0.02 wt. %, yet even more preferably less than 0.01 wt. %. Among other benefits, (e.g., anti-blocking, ink acceptance, levelling, and substrate wetting properties), when the inkjet inks of present disclosure are formulated with a fluorosurfactant (C) having a solubility in water not greater than the above listed range, the throw distance capabilities of the inkjet ink can be improved, without sacrificing dry time and decap performance.

Preferred fluorosurfactants (C) are partially fluorinated polymeric surfactants, more preferably those which are non-ionic in charge character. Of particular interest are partially fluorinated non-ionic polymeric surfactants containing one or more fluoroalkyl groups

(designated here as R_f groups) which are fluorinated, stable, inert, and non-polar, preferably saturated, monovalent, and both oleophobic and hydrophobic. The R_f groups may contain at least 1 carbon atom, preferably at least 2 carbon atoms, more preferably at least 3 carbon atoms, even more preferably at least 4 carbon atoms, yet even more preferably at least 5 carbon atoms, and up to 20 carbon atoms, preferably up to 16 carbon atoms, more preferably up to 12 carbon atoms, even more preferably up to 8 carbon atoms, yet even more preferably up to 6 carbon atoms. The R_f groups may contain straight or branched chain fluorinated alkyl groups or cyclic fluorinated alkylene groups, or combinations thereof. Each R_f group may represent a monofluoroalkyl group, a polyfluoroalkyl group, or a perfluoroalkyl group. The terminal portion of the R_f group is preferably perfluoroalkyl fragment of the formula $-C_nF_{2n+1}$ wherein n is from 3 to 20.

In preferred embodiments, the fluorosurfactant (C) is a partially fluorinated acrylic copolymer, preferably a partially fluorinated non-ionic acrylic copolymer. The partially fluorinated non-ionic acrylic copolymer may be the copolymeric reaction product formed from polymerization of one or more fluorinated (meth)acrylate monomers with one or more non-fluorinated ethylenically unsaturated monomers.

<fluorinated (meth)acrylate monomers>

The partially fluorinated non-ionic acrylic copolymer may be formed using one or more (meth)acrylate monomers containing one or more R_f groups. Examples of fluorinated (meth)acrylate monomers which may be used singly or in combination to incorporate fluoroalkyl functionality into the partially fluorinated non-ionic acrylic copolymer include, but are not limited to, $R_fCH_2OC(O)CR^1{=}CH_2$ (e.g., 2,2,3,3,4,4,4-heptafluorobutyl acrylate, 2,2,3,3,4,4,5,5-octafluoropentyl acrylate, etc.), $(R_f)_2CHOC(O)CR^1{=}CH_2$ (e.g., 1,1,1,3,3,3-hexafluoroisopropyl acrylate, etc.), $R_fCH_2CH_2OC(O)CR^1{=}CH_2$ (e.g.,

perfluorohexylethyl methacrylate, perfluorooctylethyl methacrylate, etc.),

$R_fSO_2NHCH_2CH_2OC(O)CR^1{=}CH_2$, $R_fCH_2CH_2SCH_2CH_2OC(O)CR^1{=}CH_2$,

$R_fCH_2CH_2CF_2CF_2CH_2CH_2OC(O)CR^1{=}CH_2$, $R_fCH_2CH_2(CF_2CF_2CH_2CH_2)_2OC(O)CR^1{=}CH_2$,

$R_fCH_2CF_2CH_2CH_2OC(O)CR^1{=}CH_2$, $R_fCH_2CF_2CH_2CF_2CH_2CH_2OC(O)CR^1{=}CH_2$,

$R_fOCF_2CF_2CH_2CH_2OC(O)CR^1{=}CH_2$, $R_fCHFCH_2CH_2OC(O)CR^1{=}CH_2$,

$R_fCH_2O(CH_2)_xOC(O)CR^1{=}CH_2$, $(CF_3)_2CFCH_2CH_2OC(O)CR^1{=}CH_2$,

$(CF_3)_2CFCH_2CH_2CH_2OC(O)CR^1{=}CH_2$, $R_fCH_2CH_2SO_2NHCH_2CH_2OC(O)CR^1{=}CH_2$,

$R_fCH_2CH_2SO_2N(CH_3)CH_2CH_2OC(O)CR^1{=}CH_2$,

$R_fCH_2CH_2SO_2N(CH_2CH_3)CH_2CH_2OC(O)CR^1{=}CH_2$,

$CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2CH_2OC(O)CR^1{=}CH_2$,

$R_fCH_2OC_2F_4CH_2OCH_2CH_2OC(O)CR^1{=}CH_2$,

$CH_2{=}CR^1{-}COO{-}C_2H_4{-}N(CH_3){-}SO_2{-}C_2H_4{-}R_f$ (e.g.,

2-[methyl[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)sulfonyl]amino]ethyl acrylate,

2-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-N-methyloctyl)sulfonamido)ethyl acrylate,

2-[methyl[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]ethyl methacrylate,

etc.), and $CH_2{=}CR^1{-}COO{-}C_2H_4{-}NH{-}SO_2{-}C_2H_4{-}R_f$ (e.g.,

2-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]ethyl methacrylate, etc.);

where:

R_f is a linear or branched fluoroalkyl of C_1-C_{20}, preferably a C_2 to C_6 perfluoroalkyl;

R^1 is an -H or -CH_3; and

x is an integer from 1 to 12.

<non-fluorinated ethylenically unsaturated monomers>

Non-fluorinated ethylenically unsaturated monomers used in the copolymerization reaction to form the partially fluorinated non-ionic acrylic copolymer may include, but are

not limited to, one or more of i) a non-fluorinated (meth)acrylate monomer having a polar or reactive group, ii) a non-fluorinated hydrophobic (meth)acrylate monomer, and iii) a non-fluorinated, non-acrylic ethylenically unsaturated monomer.

i) Non-fluorinated (meth)acrylate monomers having a polar or reactive group may include, but are not limited to, alkoxylated (e.g., ethoxylated) (meth)acrylates such as polyethylene glycol (meth)acrylate, polypropylene glycol (meth)acrylate, polyethylene glycol/polypropylene glycol (meth)acrylate, diethylene glycol methyl ether methacrylate, methoxy polyethylene glycol monoacrylate, triethylene glycol ethyl ether methacrylate, and 2-(2-ethoxyethoxy) ethyl acrylate; hydroxyl-containing (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, and 2-hydroxy-3-phenyloxypropyl(meth)acrylate; carboxylic acid monomers such as (meth)acrylic acid; glycidyl (meth)acrylates; amine-containing (meth)acrylates such as diethylaminoethyl (meth)acrylate and dimethylaminoethyl (meth)acrylate; and mixtures thereof.

ii) Non-fluorinated hydrophobic (meth)acrylate monomers may include, but are not limited to, linear or branched alkyl (meth)acrylates, such as butyl (meth)acrylate, sec-butyl (meth)acrylate, cetyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hexyl (meth)acrylate, isoamyl (meth)acrylate, isobutyl (meth)acrylate, lauryl (meth)acrylate, methyl (meth)acrylate, octyl (meth)acrylate, propyl (meth)acrylate, and stearyl (meth)acrylate; cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentadienyl (meth)acrylate, and t-butylcyclohexyl (meth)acrylate; aryl-containing (meth)acrylates such as phenyl (meth)acrylate and 2-phenoxyethyl (meth)acrylate; and mixtures thereof.

iii) Non-fluorinated, non-acrylic ethylenically unsaturated monomers may include, but are not limited to, vinyl esters of aliphatic acids, such as vinyl acetate, vinyl propionate, vinyl

caprylate, vinyl laurate, and vinyl stearate; allyl esters of aliphatic acids, such as allyl heptanoate, allyl acetate, allyl caprylate, and allyl caproate; styrene and alkyl styrenes, such as styrene, alpha methyl styrene, and p-methylstyrene; vinyl halides, such as vinyl fluoride, vinyl chloride, and vinyl bromide; vinylidene halides, such as vinylidene fluoride and vinylidene chloride; vinyl alkyl ketones, such as vinyl methyl ketone and vinyl ethyl ketone; vinyl ethers, such as isobutyl vinyl ether, dodecyl vinyl ether, hydroxybutyl vinyl ether, cyclohexyl vinyl ether, 4-hydroxymethyl cyclohexylmethyl vinyl ether, and octadecyl vinylether; vinylamides, such as N-vinyl-2-pyrrolidone and N-vinyl-2-caprolactam; (meth)acrylamides, such as N-methylolacrylamide, N-methylolmethacrylamide, N-cyclohexyl(meth)acrylamide, and N,N-cyclohexylmethyl(meth)acrylamide; conjugated dienes such as 1,3-butadiene, 2-chloro-1,3-butadiene, 2,3-dichloro-1,3-butadiene, and isoprene; and mixtures thereof.

The fluorosurfactant (C) may be provided in the form of a solid, for example as a pure or substantially pure material, e.g., purity of 95% or greater, preferably 99% or greater, preferably 100%. Alternatively, the fluorosurfactant (C) may be provided in the form of solvent-borne formulation, either as a suspension or solution of fluorosurfactant (C) in an appropriate organic solvent. In some embodiments, the fluorosurfactant (C) is provided in the form of a solvent-borne formulation having a content of fluorosurfactant (C) ranging from at least 1 wt. %, preferably at least 5 wt. %, preferably at least 10 wt. %, preferably at least 15 wt. %, preferably at least 20 wt. %, more preferably at least 25 wt. %, even more preferably at least 30 wt. %, yet even more preferably at least 35 wt. %, and up to 90 wt. %, preferably up to 85 wt. %, preferably up to 80 wt. %, preferably up to 75 wt. %, preferably up to 70 wt. %, preferably up to 65 wt. %, preferably up to 60 wt. %, preferably up to 55 wt. %, more preferably up to 50 wt. %, even more preferably up to 45 wt. %, yet even more preferably up to 40 wt. %, based on a total weight of the solvent-borne formulation. Any appropriate

organic solvent may be used in the solvent-borne formulation, such as those ketone solvents (B1), glycol ether solvents (B2), and/or other organic solvents described previously, with specific mention being made to ketone solvents and ester solvents (e.g., alkyl acetates).

Suitable examples of fluorosurfactants (C) that may be employed in the inkjet inks herein, include, but are not limited to CAPSTONE FS-22 (a partially fluorinated non-ionic acrylic copolymer having a solubility in water at 25 °C of less than 0.1 wt. %; solvent-borne formulation in methyl isobutyl ketone, 30 wt. % active solution) and CAPSTONE FS-83 (a partially fluorinated non-ionic acrylic copolymer having a solubility in water at 25 °C of less than 0.1 wt. %; solvent-borne formulation in n-butyl acetate, 35 wt. % active solution), each available from Chemours.

As will become clear, it has been unexpectedly discovered that a specific type of fluorosurfactant (C)—those having a solubility in water at 25 °C of less than 0.1 wt. %, and preferably those of the partially fluorinated non-ionic acrylic copolymer variety—provides inkjet inks with long throw distance capabilities, e.g., up to 10 mm.

On the other hand, it has been found that water-soluble fluorosurfactants (i.e., those having a solubility in water at 25 °C of greater than or equal to 0.1 wt. %), including those fluorosurfactants employed previously in inkjet inks (*see* e.g., US8778074 and US9957401—each incorporated herein by reference in its entirety), fail to provide acceptable throw distances. Examples of such water-soluble fluorosurfactants include, but are not limited to,

- non-ionic fluorosurfactants, including ethoxylated non-ionic fluorosurfactants (e.g., those of the general formula $R_fC_2H_4O(C_2H_4O)_yH$), such as CAPSTONE FS-30 (an ethoxylated non-ionic fluorosurfactant having a solubility in water at 25 °C of greater than or equal to 0.1 wt. %; water-borne formulation, 25 wt. % active in water), CAPSTONE FS-31 (a non-ionic fluorosurfactant having a solubility in water at 25 °C

of greater than or equal to 0.1 wt. %; water-borne formulation, 25 wt. % active in water), and CAPSTONE FS-3100 (a non-ionic fluorosurfactant having a solubility in water at 25 °C of greater than or equal to 0.1 wt. %; solid), each available from Chemours, as well as ZONYL FSO-100 (an ethoxylated non-ionic fluorosurfactant having a solubility in water at 25 °C of greater than or equal to 0.1 wt. %) and ZONYL FSN (an ethoxylated non-ionic fluorosurfactant having a solubility in water at 25 °C of greater than or equal to 2 wt. %), each previously available from E. I. du Pont de Nemours and Company, now discontinued;

- amphoteric fluorosurfactants, such as CAPSTONE FS-50 (a betain partially fluorinated surfactant having a solubility in water at 25 °C of greater than or equal to 0.1 wt. %; 27 wt. % active in water/ethanol), available from Chemours; and
- anionic fluorosurfactants, such as CAPSTONE FS-63 (an anionic fluorosurfactant having a solubility in water at 25 °C of greater than or equal to 0.1 wt. %; 35 wt. % active in isopropanol/water), available from Chemours.

Rosin resin (D)

The inkjet inks may be optionally formulated with a rosin resin (D). Any rosin resin (D) that is compatible with the resin (A), the ketone solvent (B1), and the fluorosurfactant (C) may be utilized herein, including rosin resins (D) derived from gum rosin, wood rosin, and tall oil rosin (the main components of which are resin acids such as abietic acid, palustric acid, neoabietic acid, pimaric acid, isopimaric acid and/or dehydroabietic acid), preferably rosin resins (D) derived from wood rosin. When employed, the rosin resin (D) may be used in an amount of up to 10 wt. %, for example at least 0.1 wt. %, preferably at least 0.2 wt. %, preferably at least 0.4 wt. %, more preferably at least 0.6 wt. %, more preferably at least 0.8 wt. %, even more preferably at least 1 wt. %, yet even more preferably at least 1.5 wt. %, and

up to 10 wt. %, preferably up to 8 wt. %, more preferably up to 6 wt. %, even more preferably up to 4 wt. %, yet even more preferably up to 2 wt. %, based on a total weight of the inkjet ink. When the inkjet inks are formulated with rosin resin (D), it is preferred that the amount (in terms of weight %) of rosin resin (D) is less than or equal to the amount of resin (A).

The rosin resin (D) may be formed by modifying the aforementioned rosins through esterification, hydrogenation (including partial hydrogenation), dimerization, and/or other modifications/functionalization for example through Diels-Alder reaction with an unsaturated di-acid (e.g., maleic or fumaric acid/anhydride), carboxylic acid reduction to the respective aldehydes/alcohols, double bond isomerization, dehydrogenation, oxidation, disproportionation, and the like. Exemplary rosin resins (D) include, but are not limited to:

- a rosin ester resin, such as e.g., an ester of a rosin composed mainly of an abietic type or pimaric type resin acid that has been reacted with an alcohol(s) such as glycerin, pentaerythritol, ethylene glycol, diethylene glycol, triethylene glycol, methanol, etc., and optionally hydrogenated or partially hydrogenated, with specific mention being made to HARIESTER products available from Harima Chemicals, Inc., STAYBELITE ESTER 10-E and PERMALYN 6110, each available from Eastman, SUPER ESTER A-125, SUPER ESTER A-75, PENSEL D-125, PINECRYSTAL KE-359 available from Arakawa Chemical Industries, Ltd., and FORAL 85, FORAL 105, HERCOLYN products, PEXALYN products, and PENTALYN products available from Pinova;
- a hydrogenated acidic rosin such as FORAL AX and FORAL DX, each available from Pinova
- a partially hydrogenated acidic rosin such as STAYBELITE RESIN-E, available from Eastman, and STAYBELITE and STAYBELITE A, each available from PINOVA;

- a dimerized rosin such as POLY-PALE partially dimerized rosin available from Eastman; and
- a functionalized rosin resin, for example an ester (e.g., glycerol ester) of a rosin which has been modified with maleic anhydride or a rosin which has been subject to carboxylic acid reduction conditions, with specific mention being made to LEWISOL 28-M and Abitol-E hydroabietyl alcohol, each available from Eastman;
- and mixtures thereof.

In some embodiments, the rosin resin (D) has a softening point (ring-and-ball SP) of at least 50 °C, preferably at least 55 °C, more preferably at least 60 °C, even more preferably at least 65 °C, and up to 80 °C, preferably up to 75 °C, more preferably up to 70 °C, even more preferably up to 68 °C. In some embodiments, the rosin resin (D) is an acidic rosin (non-esterified) and has an acid number (in mg KOH/g) of at least 100, preferably at least 110, more preferably at least 120, more preferably at least 130, even more preferably at least 140, yet even more preferably at least 150, and up to 170, preferably up to 165, more preferably up to 160, even more preferably up to 158.

In preferred embodiments, the rosin resin (D) is a hydrogenated acidic rosin, preferably a hydrogenated acidic wood rosin, for example FORAL AX and FORAL DX, each available from Pinova. In some embodiments, the inkjet inks are substantially free of rosin resins (D). In some embodiments, the inkjet inks are substantially free of rosin ester resins, partially hydrogenated acidic rosins, dimerized rosins, and other functionalized/modified rosin resins. In some embodiments, a hydrogenated acidic rosin is the only rosin resin (D) present in the inkjet inks.

Other binder resins

In addition to the resin (A), and any optional rosin resin (D), the inkjet inks may optionally contain other binder resins/tackifiers/adhesive substances in an amount of at least 0.1 wt. %, preferably at least 0.5 wt. %, preferably at least 1 wt. %, more preferably at least 1.5 wt. %, even more preferably at least 2 wt. %, yet even more preferably at least 2.5 wt. %, and up to 10 wt. %, preferably up to 9 wt. %, preferably up to 8 wt. %, preferably up to 7 wt. %, preferably up to 6 wt. %, more preferably up to 5 wt. %, even more preferably up to 4 wt. %, yet even more preferably up to 3 wt. %, based on a total weight of the inkjet ink. Such additional resins, binders, tackifiers, or adhesive substances may include, but are not limited to,

- phenol resins (i.e. copolymers of phenolic compounds with formaldehyde), for example novolak resins such as PHENOLITE TD-2131 and PHENOLITE TD-2090 available from DIC Corp.;
- polyamide resins, for example VERSAMID 725, 744, 756, 759 available from BASF Japan Ltd., TOHMIDE 90, 92, 394-N available from Sanho Chemical Co. Ltd., and SUNMIDE 550, 554, 615A, 638, 640 available from Evonik;
- epoxy resins including sulfonamide-modified epoxy resins for example AD-PRO MTS available from Rit-Chem;
- (meth)acrylate and styrene/(meth)acrylate resins for example JONCRYL 63, JONCRYL 67, JONCRYL 586, JONCRYL 611, JONCRYL 682, JONCRYL 693, available from BASF, PARALOID DM-55 and PARALOID B-66, available from Palmer Holland, PARALOID B-72, available from Dow Chemical, USA, and ELVACITE 2013, available from Lucite Inc.;
- polyurethane resins, such as those formed from reaction between (i) polyols including, but not limited to, ethylene glycol, propylene glycol, propanediol, butanediol, polyethylene glycol, polypropylene glycol, polytetrahydrofuran diol,

3-methyl-1,5-pentanediol, 1,9-nonanediol, polyester polyols such as polyethylene glycol adipate diol, polyethylene glycol succinate diol, poly(3-methyl-1,5-pentanediol adipate) glycol, poly(3-methyl-1,5-pentanediol terephthalate) glycol, carbonate polyols, and (ii) diisocyanates including, but not limited to, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4-diphenylmethane diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate; for example PERMAX 200, PERMAX 202, and SANCURE 20025F, available from Lubrizol;

- polyvinyl butyral resins, for example PIOLOFORM BN 16 and MOWITAL B20H available from Kuraray America, Inc.;
- polyhydroxystyrene resins such as poly(p-hydroxy styrene) from DuPont;
- vinyl resins, for example UCAR VYHH, VMCH, VMCA, and VAGF, available from Dow Chemical Company, and VINNOL E15/45, H14/36, E15/45M, and E16/40A, available from Wacker Chemie AG, Germany;
- formaldehyde resins, including sulfonamide modified formaldehyde resins such as p-toluene sulfonamide formaldehyde resin, melamine formaldehyde resins, sulfonamide-modified melamine formaldehyde resins;
- cellulose ester resins such as cellulose acetate butyrate (CAB-551-0.01) available from Eastman;
- as well as polyesters, sulfonated polyesters, gums, cellulose ethers, cellulose nitrate resins, polymaleic anhydrides, acetal polymers, styrene/butadiene copolymers, ketone-aldehyde resins, and polyketone resins;
- and the like, including mixtures thereof.

In some embodiments, other than the resin (A), and any optional rosin resin (D), the inkjet inks are substantially free of additional binder resins/tackifiers/adhesive substances, such as those mentioned above. In some embodiments, the inkjet inks contain a combination

of the resin (A) and the rosin resin (D), and are preferably substantially free of additional resins, binders, tackifiers, or adhesive substances.

(E) Colorant

It is to be readily appreciated by those of ordinary skill in the art that one or more colorants (E) may be optionally included in the inkjet inks to provide colored inks that may be used for a variety of printing purposes and the inkjet inks are not limited to any particular color. Any colorant (E) can be employed in the inkjet inks to provide the desired color, including dyes, pigments, mixtures thereof, and the like, provided that the colorant (E) can be dissolved or dispersed within the inkjet inks. Suitable colors include, for example, cyan, magenta, yellow, and key (black) ("CMYK"), white, orange, green, light cyan, light magenta, violet, and the like, including both spot colors and process colors. In general, the colorants (E) may be employed in amounts of at least 0.1 wt. %, preferably at least 0.5 wt. %, more preferably at least 1 wt. %, even more preferably at least 2 wt. %, yet even more preferably at least 3 wt. %, and up to 20 wt. %, preferably up to 15 wt. %, more preferably up to 10 wt. %, even more preferably up to 8 wt. %, yet even more preferably up to 7 wt. %, based on a total weight of the inkjet inks.

The inkjet inks can be formulated with various dyes, with particular preference given to organic dyes such as OIL BLACK 860, available from Orient Chemical Industries, and metal complex dyes.

The inkjet inks can be formulated with various inorganic pigments and/or organic pigments. In addition to providing color to the inkjet inks, such pigments may be capable of improving the light resistance, the weather resistance, etc., of the printed images.

(F) Additive(s)

In addition to the components already mentioned, the inkjet inks may also optionally be formulated with various additives (F) to improve various ink characteristics and performance. For example, the inkjet inks may optionally contain one or more of an anti-kogation agent, a stabilizer, a humectant, a security taggant, and an additional surfactant (i.e., in addition to the fluorosurfactant (C)) in art appropriate levels as known by those of ordinary skill in the art.

With respect to the additional surfactant, additional surfactants are contemplated for use in the disclosed inkjet inks, so long as their optional use is to be accompanied by the fluorosurfactant (C) described as suitable above. Examples of additional surfactants include, but are not limited to,

- polysiloxanes including organomodified silicones (e.g., alkyl, aryl, and/or arylalkyl modified silicones) such as SILTECH C-32, available from Siltech Corporation, COATOSIL 1211C and 3573, each available from Momentive, KF-410 (an arylalkyl-modified polydimethylsiloxane), available from Shin-Etsu Chemical Co., and BYK-322 and BYK-323 (arylalkyl-modified poly(dimethylsiloxane-co-methylalkylsiloxane)), each available from BYK Additives & Instruments;
- silicone acrylate copolymers such as KP-541, KP-543, KP-545, KP-550, and KP-575 (acrylic polymers grafted with polydimethylsiloxane side chains, available from Shin-Etsu Chemical Co., Ltd.), and BYK-3550 (available from BYK Japan K.K.);
- polyether modified silicones, including those which are block copolymers having a pendent graft structure formed from a linear or branched polydimethylsiloxane backbone containing one or more polyether side chains and optionally one or more fatty alkyl side chains, such as KF-6013 (PEG-9 dimethicone, uncapped, HLB = 10.0), KF-6015 (PEG-3 dimethicone, uncapped, HLB = 4.5), KF-6017 (PEG-10

dimethicone, uncapped, HLB = 4.5), and KF-6038 (Lauryl PEG-9 polydimethylsiloxyethyl dimethicone, uncapped, HLB = 3.0), each available from Shin-Etsu Chemical Co.;

- photo-cross-linkable silicone acrylates or silicone polyether acrylates such as TEGO RAD 2100, TEGO RAD 2200, TEGO RAD 2250, TEGO RAD 2300 (silicone polyether acrylate), each available from Evonik Industries, and BYK-UV 3500 and 3530, available from BYK;-
- polyacrylates including polyacrylate copolymers and cross-polymers such as BYK-381 and BYK-361N (polyacrylate copolymer), each available from BYK, PEMULEN EZ-4U (acrylate/C10-C30 alkyl acrylate crosspolymer) and PEMULEN TR-2 (acrylic acid/C10-C30 alkyl acrylate crosspolymer), each available from Lubrizol;
- acetylenic diol and acetylenic glycol-based gemini surfactants such as SURFYNOL SEF and DYNOL surfactants, available from Evonik Industries;
- polysiloxane-based gemini surfactants such as TEGO TWIN 4100, available from Evonik Industries;
- non-ionic polyethers for example as substrate wetting surfactants such as TEGO WET 510 (hydrophilic polyether substrate wetting surfactant), available from Evonik Industries;
- amides or monoalkanolamides of fatty acids, including alkoxylated monoalkanolamides of fatty acids such as coconut fatty acid monoethanolamide and coconut fatty acid monoethanolamide reacted with 2-20 moles of ethylene oxide;
- ethers, such as alkoxylated C_1-C_{22} alcohols including alkoxylated fatty alcohols such as BIO-SOFT N-600 (C12-C13 alcohol ethoxylate), MAKON DA-4 (ethoxylated isodecyl alcohol), MERPOL SE (alcohol ethoxylate), and POLYSTEP TD-6

(ethoxylated tridecyl alcohol), each available from Stepan, ethylene oxide/propylene oxide copolymers, alkoxylated alkylphenols, and alkyl polyglycosides (APGs) such as those made from reaction between fatty alcohols and glucose;

- fatty esters such as ethoxylated and/or propoxylated fatty acids (e.g., castor oil with 2 to 40 moles of ethylene oxide), alkoxylated glycerides (e.g., PEG-24 glyceryl monostearate), glycol esters and derivatives, monoglycerides, polyglyceryl esters, esters of polyalcohols, and sorbitan/sorbitol esters like sorbitan monolaurate (e.g., EMASOL L-10V, available from Kao) and polysorbates including mono-, bi- or tri-fatty acid esterified polysorbates such as TOXIMUL SEE-340 (sorbitan trioleate ethoxylate (20)), available from Stepan; and
- glycosides of fatty alcohols such as PLANTASENS NATURAL EMULSIFIER HE20 (cetearyl glucoside, sorbitan olivate), available from Clariant.

In preferred embodiments, the inkjet inks of the present disclosure are substantially free of additional surfactants, such as those listed above.

Methods of Making

Embodiments of the inkjet inks described herein may be prepared by any suitable technique known to those of ordinary skill in the art, for example by combining components (A) a resin, (C) a fluorosurfactant, and any desired optional ingredients (e.g., (D) a rosin resin, (E) a colorant, and/or an additive (F)) with a suitable solvent system (B) comprising (B1) a ketone solvent and optionally (B2) a glycol ether, in any order and stirring, agitating, and/or homogenizing at a temperature between 20 and 100°C for a suitable amount of time to form a homogeneous solution.

In one example, the inkjet ink may be made by first combining the resin (A) and the fluorosurfactant (C) with the ketone solvent (B1), and any optional resins (e.g., (D) a rosin

resin) or other optional additive(s) (F) in a vessel, followed by stirring for at least 10 minutes, preferably at least 15 minutes, preferably at least 20 minutes, preferably at least 25 minutes, preferably at least 30 minutes, preferably at least 35 minutes, preferably at least 40 minutes, preferably at least 45 minutes. Glycol ether (B2), when employed, may then be added to the resulting mixture, and subsequently stirred for at least 10 minutes, preferably at least 15 minutes, preferably at least 20 minutes, preferably at least 25 minutes. The colorant (E) may then be added as the final component with continued mixing, and the solution may then be mixed for at least 10 minutes, preferably at least 15 minutes, preferably at least 20 minutes, preferably at least 25 minutes, preferably at least 30 minutes, preferably at least 35 minutes, preferably at least 40 minutes, preferably at least 45 minutes to afford the inkjet ink. The resulting inkjet ink may then be placed into a printing cartridge, such as e.g., a FUNAI TIJ cartridge made by Funai Co., or other printhead suitable for ketone-based ink.

Properties

Among other advantages, the inkjet inks disclosed herein are characterized by having long throw distance capabilities, while also possessing a superior combination of extended decap times and quick dry times after being applied.

Dry times may be measured by applying the inkjet inks in the form of a solid block image (e.g., 1 cm * 10 cm) onto a substrate, waiting for the inkjet inks to dry under ambient conditions (in air at room temperature, about 23°C, without applied heat), for a certain period of time, for example at 5, 10, 15, 20, 25, or 30 seconds, and then performing an abrasion test by finger to test if color transfers from the printed image to the finger at the tested time interval. If color transfer occurs, then the tested dry time is not satisfactory to achieve complete drying (rated "fail"). If no color transfer occurs, then the tested dry time is satisfactory to achieve complete drying (rated "pass"). Any inkjet inks requiring dry times of

over 30 seconds to achieve a "pass" rating are considered unacceptable/slow drying ("Not Good"), while those which achieve a "pass" rating with dry times of 30 seconds or less are deemed acceptable/quick drying ("Good"). In preferred embodiments, the inkjet inks of the present disclosure have acceptable/quick dry times ("Good" rating), and dry within 30 seconds or less, preferably 25 seconds or less, preferably 20 seconds or less, more preferably 15 seconds or less, even more preferably 10 seconds or less, yet even more preferably 5 seconds or less, after being applied.

The inkjet inks disclosed herein also possess extended decap times, for example as measured by printing a narrow line picture (e.g., barcode) (1 mm * 1 cm, narrow lines, Monochrome bitmap), exposing the inkjet ink to air (decapping the ink cartridge) for a particular time (e.g., 30 seconds, 1 minute, 10 minutes, etc.), reprinting the same narrow line image, and comparing the reprinted image after decapping to the original image to determine if loss of lines/loss of line clarity occurs in the narrow line image. If no loss of lines/loss of line clarity occurs at the tested time interval, then the inkjet inks are given a "Good" decap rating for that time interval. If 1-2 lines are lost/lost clarity at the tested time interval, but not enough to significantly affect the clarity or readability of the narrow line image, then the inkjet inks are given an "Acceptable" decap rating for that time interval. If more than 2 lines are lost/lost clarity at the tested time interval, then the inkjet ink is classified as "Not Good" at that time interval. Suitable inkjet inks are those which can be decapped for time intervals of 30 seconds, 1 minute, and 10 minutes, and achieve an "Acceptable" or "Good" decap classification when decapped (i.e., exposed to air) for each of the tested time intervals. Preferred inkjet inks are those which maintain a "Good" decap rating when decapped for 30 seconds or longer, preferably 1 minute or longer, more preferably 10 minutes or longer, even more preferably 30 minutes or longer, yet even more preferably 60 minutes or longer.

The throw distance of an inkjet ink may be measured by printing a test pattern with increasing distances between the printhead and the substrate and assessing the quality of the image at each distance. This may include printing an image such as an alphanumeric sequence at various throw distances (e.g., 2 mm, 4 mm, 6 mm, 8 mm, and 10 mm) and visually assessing the quality of printed image in terms of image clarity, edge definition, and accuracy of drop placement. If the printed image is clearly readable, with well-defined edges and accurate drop placement, then the inkjet inks are given a "Good" throw distance rating for that tested throw distance. If the printed image is readable, but has some haziness, slight loss of edge definition, and/or slight loss of drop placement accuracy, then the inkjet inks are given an "Acceptable" throw distance rating for that tested throw distance. If the printed image is not readable, because the images lack clarity, have poor edge definition and/or inaccurate drop placement, then the inkjet inks are given a "Not Good" throw distance rating for that tested throw distance. Preferred inkjet inks are those which maintain a "Good" or "Acceptable" throw distance evaluation for throw distances of at least 1 mm, preferably at least 2 mm, preferably at least 3 mm, preferably at least 4 mm, preferably at least 5 mm, preferably at least 6 mm, preferably at least 7 mm, more preferably at least 8 mm, even more preferably at least 9 mm, yet even more preferably at least 10 mm, and up to 15 mm, preferably up to 14 mm, preferably up to 13 mm, preferably up to 12 mm.

Printed Article

The inkjet inks can be printed on various substrates including three dimensional parts as well as flat sheets or webs that are supplied in roll form, for the manufacture of a wide variety of printed articles. While flat substrates are suitable substrates for forming printed articles, a particular advantage of the present disclosure is that the disclosed inkjet inks—having long throw distance capabilities—enable printed images to be formed on

complex three dimensional substrates, such as those which are radial, curved, serrated, corrugated, fluted, lipped, and/or those which have a structured surface (e.g., grained surface), all of which are notoriously difficult substrates owing to the long distance that the ink must travel to reach all parts of the complex surface. The printed articles may be suitable in the graphic arts, textiles, packaging (e.g., food packaging, pharmaceutical packaging, etc.), lottery, direct mail, business forms and publishing industries, examples of which include a tag or label, a lottery ticket, a publication, packaging (e.g., food packaging, pharmaceutical packaging, blister packaging, other various flexible packing, etc.), a folding carton, a rigid container (e.g., a plastic cup or tub, glass containers, metal cans, bottles such as PET bottles, jars, and tubes), envelopes, corrugate, a point-of-sale display, and the like. Particularly preferred printed articles are those having a dried form of the inkjet ink disposed on a complex three dimensional part of the printed article, for example, where the printed image is located on a fluted or corrugated portion of a plastic container, or on the concave dome-shaped bottom of a metal can.

The inkjet inks may be printed on porous (or penetrable) substrates, examples of which include, but are not limited to, non-coated paper, wood, membranes, corrugate (corrugated cardboard/fiberboard), and fabrics (including, for example, but not limited to, woven fabric, non-woven fabric, and foil-laminated fabric).

The inkjet inks may also be printed on non-porous (or non-penetrable substrates), for example, various plastics, glass, metals (e.g., steel, aluminum, etc.), and/or non-penetration papers (e.g., coated papers such as varnish coated papers), including, but not limited to, molded plastic or metal parts as well a flat sheets or rolls of plastic or metallic films. Examples include those substrates containing polyesters such as polyethylene terephthalate (PET), biaxially oriented polystyrene (OPS), polyolefins such as polyethylene (PE), polypropylene (PP), oriented polypropylene (OPP), and biaxially oriented polypropylene

(BOPP), polylactic acid (PLA), nylon and oriented nylon, polyvinyl chloride (PVC), cellulose triacetate (TAC), polycarbonate, acrylonitrile butadiene styrene (ABS), polyacetal, polyvinyl alcohol (PVA), coated papers such as varnish coated papers, and metals such as steel and aluminum, and the like.

Method of Forming a Printed Image

With inkjet printing, a desired printed image is formed when a precise pattern of dots is ejected from a drop-generating device, known as a printhead, onto a print medium. The printhead has an array of precisely formed nozzles located on a nozzle plate and attached to an inkjet printhead substrate. The inkjet printhead substrate incorporates an array of firing chambers that receive inkjet ink through fluid communication with one or more ink reservoirs. Each firing chamber has a resistor element, known as a firing resistor, located opposite the nozzle so that the inkjet ink collects between the firing resistor and the nozzle. Each resistor element is typically a pad of a resistive material and measures for example about 35 μm × 35 μm. The printhead is held and protected by an outer packaging referred to as a print cartridge or an inkjet pen. Upon energizing of a particular resistor element, a droplet of inkjet ink is expelled through the nozzle toward the print medium. The firing of ink droplets is typically under the control of a microprocessor, the signals of which are conveyed by electrical traces to the resistor elements, forming alphanumeric and other image patterns on the print medium. Since the nozzles are small, typically 10 μm to 40 μm in diameter, inks that minimize clogging are desired. In particular, since thermal inkjet (TIJ) is an open atmosphere print head design (the nozzle orifices are open to atmosphere and there is no valve seal at the orifice to allow ink pressurization), TIJ printing has historically suffered from poor performance during intermittent printing, where decap time (print idle time) causes premature drying of ink in and around the nozzles.

The present disclosure provides a method of forming a printed image by applying the inkjet ink, in one or more of its embodiments, onto a surface of a substrate by a thermal inkjet printhead and allowing the inkjet ink to dry. Use of the inkjet inks described herein overcomes the competing problems of short decap time (rate of solvent loss is too fast) and slow drying times (rate of solvent loss is too slow) commonly associated with thermal inkjet processes, while also enabling application of inkjet inks from greater throw distances than can be traditionally achieved with inkjet printing systems.

Any drop on demand printhead known to those of ordinary skill in the art of inkjet printing can be used as printing units in the present method, including continuous printheads, thermal printheads, electrostatic printheads, and acoustic printheads, preferably a thermal printhead (having a thermal transducer) is used. Typical parameters, such as, for example, printing resolution, printing speed, printhead pulse warming temperature, driving voltage and pulse length, can be adjusted according to the specifications of the printhead. Printheads which are generally suitable for usage in the methods herein have a droplet size in the range of 2 to 80 pL and a droplet frequency in the range of 10 to 100 kHz, and high quality prints may be obtained for example by setting the driving voltage to 8.0 to 9.5 Volts, the print speed up to 300 feet/minute, the pulse warming temperature to 25 to 45°C, and the pulse length to 0.7-2.5 microseconds, although values above or below these described may also be used and still obtain satisfactory prints. One non-limiting printhead example suitable for use in the disclosed methods is FUNAI TIJ cartridge made by Funai Co.

After application, the inkjet ink is dried. In preferred embodiments, drying is achieved by allowing the applied inkjet ink to dry under ambient conditions (in air, at about 23°C) for 30 seconds or less, preferably 25 seconds or less, more preferably 20 seconds or less, even more preferably 15 seconds or less, yet even more preferably 10 seconds or less.

While external heat may be applied to dry the applied inkjet inks, in preferred embodiments, external heat is not applied to facilitate drying or to increase drying speeds. For example, a heater is preferably not employed for drying the inkjet ink after application. Furthermore, the methods of the present disclosure do not require energy curing (e.g., UV or electron beam curing). Once the applied ink is deemed dry, further coatings of inkjet ink may be applied, or any processing steps known to those of ordinary skill in the art may be performed as desired.

It should also be recognized that substrate surface treatments such as corona treatment, atmospheric plasma treatment, and flame treatment may optionally be employed in the methods herein prior to application of the inkjet inks to improve printed article characteristics, for example ink adhesion. The parameters of such substrate surface treatments may be varied greatly depending on the substrate material to be printed, the specific inkjet ink utilized, the printing method applied, and the desired properties and applications of the printed article.

The examples below are intended to further illustrate the inkjet inks and are not intended to limit the scope of the claims.

EXAMPLES

Materials

Glycol ether PM is propylene glycol monomethyl ether (b.p. 120 °C). Glycol ether PnP is propylene glycol mono-n-propyl ether (b.p. 149 °C). PICCOLYTE A135 is a terpene resin made from α-pinene (ring-and-ball SP = 132-138 °C, bromine number = 27), available from Pinova. YS POLYSTER U115 is a terpene phenol resin (OHV = 30 mgKOH/g; SP = 115 °C), available from Yasuhara Chemical Co. Ltd. FORAL AX is a rosin resin (a hydrogenated acidic wood rosin), available from Pinova. OIL BLACK 860 is an organic dye,

available from Orient Chemical Industries. The fluorosurfactants used in the Examples are presented in Table 1.

Table 1. Fluorosurfactants

Fluorosurfactant	Water solubility [a]	Ionic character	Description	Formulation	Active content
CAPSTONE FS-22	Water-insoluble	Non-ionic	Partially fluorinated acrylic copolymer	Solvent-borne in methyl isobutyl ketone	30 wt. %
CAPSTONE FS-83	Water-insoluble	Non-ionic	Partially fluorinated acrylic copolymer	Solvent-borne in n-butyl acetate	35 wt. %
CAPSTONE FS-30	Water-soluble	Non-ionic	Ethoxylated fluorosurfactant	Water-borne	25 wt. %
CAPSTONE FS-31	Water-soluble	Non-ionic	Fluorosurfactant	Water-borne	25 wt. %
CAPSTONE FS-50	Water-soluble	Amphoteric	Betain partially fluorinated surfactant	Solution in water/ethanol	27 wt. %
CAPSTONE FS-63	Water-soluble	Anionic	Fluorosurfactant	Solution in isopropanol/ water	35 wt. %
CAPSTONE FS-3100	Water-soluble	Non-ionic	Fluorosurfactant	Solid	100 wt. %

[a] 0.1 wt. % concentration of pure fluorosurfactant in water at 25 °C

To determine fluorosurfactant solubility, solid fluorosurfactants were either obtained from a commercial supplier, or, if fluorosurfactants were commercially available as solutions, then the fluorosurfactant solutions were completely dried under 60°C to provide the fluorosurfactants as pure solids.

The solid fluorosurfactants were then added to water at 25 °C at a concentration of 0.1 wt. %, and visually inspected for dissolution. If the solid fluorosurfactant clearly dissolved in

water at a 0.1 wt. % concentration, then it was determined to be water-soluble—and if not, then it was determined to be water-insoluble. The water-solubility testing results are shown in Table 1.

Inkjet ink evaluation methods

Printing sample preparation

The inkjet ink examples were evaluated through a FUNAI TIJ cartridge made by Funai Co. Thermal printing technology related to FUNAI was used to evaluate the inks (Software and hardware made by XiJet, Transport table made by Kirk Rudy).

Dry time evaluation

For evaluating dry times, the printing conditions utilized were as follows:

- Printing substrate; varnish coated paper
- Printing resolution; 600 dpi * 300 dpi (vertical*horizontal)
- Printing speed; 100 feet/minute
- Pre Fire 450 nsec
- Dead Time 1700 nsec
- Main Fire 1400 nsec
- Voltage 9.0 V
- Temperature 30°C
- Printing image; 100% duty (1 cm * 10 cm, Monochrome bitmap, solid block image)

The abrasion test was done by the finger after specific time passed (5, 10, 15, 20, 25, and 30 sec). A colored finger indicates not enough time has lapsed for complete drying ("fail"), and a non-colored finger indicates the time is adequate for complete drying ("pass"). Inkjet inks with a dry time of over 30 seconds to achieve a "pass" rating were deemed

unacceptable/slow drying ("Not Good"), while those which achieve a "pass" rating with dry times of 30 seconds or less are deemed acceptable/quick drying ("Good").

Decap time evaluation

For evaluating decap times, the printing conditions utilized were as follows:

- Printing substrate; normal (non-coated) paper
- Printing resolution; 300 dpi * 300 dpi (vertical*horizontal)
- Printing speed; 100 feet/minute
- Pre Fire 450 nsec
- Dead Time 1700 nsec
- Main Fire 1400 nsec
- Voltage 9.0 V
- Temperature 30°C
- Printing image; 100% duty (1 mm * 1 cm, Monochrome bitmap, narrow line image)

The narrow line image was printed to confirm that there were no missing or unclear lines included in the printed image (signifying plugged or missing nozzles). After confirming, the printhead was left decapped for a specific time (30 seconds, 1 min, or 10 min), then reprinted using the same narrow line image. The reprinted narrow line image (after the specific time lapse) was checked to determine whether loss of lines/loss of line clarity occurred. If no loss of lines/loss of line clarity occurred, then the inkjet inks were given a "Good" decap rating for that time interval. If 1-2 lines were lost/lost clarity at the tested time interval, but not enough to significantly affect the clarity or readability of the narrow line image at the tested time interval, then the inkjet inks were given an "Acceptable" decap rating for that time interval. If more than 2 lines were lost/lost clarity at the tested time interval, then the inkjet inks were classified as "Not Good" at that time interval. Suitable/desirable inkjet

inks are those which achieve a, "Acceptable" or "Good" decap classification when decapped (i.e., exposed to air) for each of the tested time intervals.

Throw distance evaluation

For evaluating the throw distance, the printing conditions utilized were as follows:

- Printing substrate; normal (non-coated) paper
- Printing resolution; 300 dpi * 300 dpi (vertical*horizontal)
- Printing speed; 100 feet/minute
- Pre Fire 450 nsec
- Dead Time 1700 nsec
- Main Fire 1400 nsec
- Voltage 9.0 V
- Temperature 30°C
- Tested distance between printhead and substrate (throw distance); 2 mm, 4 mm, 6 mm, 8 mm, 10 mm
- Printing image; 100% duty (*see* e.g., the FIGURE)
    - Alphanumeric sequence which reads:

Kao Collins Inc.
1201 Edison Drive,
Cincinnati, OH 45216

The alphanumeric sequence was printed onto the substrate at the various tested throw distances, and the resulting printed images were visually evaluated for image quality at the tested throw distance and rated according to Table 2. Suitable/desirable inkjet inks are those which achieve a "Good" or "Acceptable" throw distance evaluation for each tested throw distance.

Table 2. Throw distance evaluation

Throw distance evaluation	Description	Image quality outcome
Good	Clear images; well-defined edges; accurate drop placement	Clearly readable
Acceptable	Images were mostly clear but with some haziness; slight loss of edge definition and drop placement accuracy	Readable
Not Good	Images lacked clarity; poor edge definition; inaccurate drop placement	Not readable

Inkjet ink Examples

Example inkjet inks are given in Table 3 below. The amount of each component is expressed in terms of weight percentage relative to a total weight (100%) of the inkjet ink. * denotes the example is a comparative example.

Preparation methods

To prepare the example inks, the resin(s) and any fluorosurfactant were first combined with methyl ethyl ketone (MEK), and mixed by mechanical stirrer for at least 30 minutes. Then the glycol ethers were added into the mixture and mixed for at least 15 minutes. The dye was then added into the mixture and mixed for at least 30 minutes to obtain the inkjet inks. The inkjet ink examples were then evaluated through a FUNAI TIJ cartridge made by Funai Co.

Table 3. Inkjet Ink Examples 1-12

	Ex 1	Ex 2	Ex 3*	Ex 4*	Ex 5*	Ex 6*	Ex 7*	Ex 8*	Ex 9	Ex 10*	Ex 11	Ex 12
Methyl ethyl ketone	71.00	71.00	71.00	71.00	71.00	71.00	72.50	73.00	72.95	68.00	71.00	72.00
Glycol ether PM	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Glycol ether PnP	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
PICCOLYTE A135	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-	1.00
YS POLYSTER U115	-	-	-	-	-	-	-	-	-	-	1.00	-
FORAL AX	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-
CAPSTONE FS-22 (wt. % active)	2.00 (0.60)	-	-	-	-	-	-	-	0.05 (0.015)	5.00 (1.50)	2.00 (0.60)	2.00 (0.60)
CAPSTONE FS-83 (wt. % active)	-	2.00 (0.70)	-	-	-	-	-	-	-	-	-	-
CAPSTONE FS-30 (wt. % active)	-	-	2.00 (0.50)	-	-	-	-	-	-	-	-	-
CAPSTONE FS-31 (wt. % active)	-	-	-	2.00 (0.50)	-	-	-	-	-	-	-	-
CAPSTONE FS-50 (wt. % active)	-	-	-	-	2.00 (0.54)	-	-	-	-	-	-	-
CAPSTONE FS-63 (wt. % active)	-	-	-	-	-	2.00 (0.70)	-	-	-	-	-	-
CAPSTONE FS-3100	-	-	-	-	-	-	0.50	-	-	-	-	-
OIL BLACK 860	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Inkjet ink performance

As can be seen in Table 4, when a water-insoluble (solubility in water at 25 °C of less than 0.1 wt. %) fluorosurfactant was used in combination with methyl ethyl ketone and either a terpene resin or terpene phenol resin, remarkable effects were achieved in terms of throw distance, dry times, and decap times (Examples 1, 2, 9, 11, and 12). In particular, such inkjet inks formulated with a partially fluorinated non-ionic acrylic copolymer provided readable images even at the highest throw distance tested (10 mm), which is a significant achievement for thermal inkjet printing.

Conversely, inkjet inks which contained no fluorosurfactant (Example 8), or a water-soluble (solubility in water at 25 °C of greater than or equal to 0.1 wt. %) fluorosurfactant (Examples 3-7) suffered from unacceptable decap behavior, and inferior throw distances. Specifically, Example 8 which lacked fluorosurfactant altogether, was quick drying, but was given a "Not Good" decap classification at each tested time interval, and provided poor image quality at each throw distance evaluated. Of the inkjet inks formulated with a water-soluble fluorosurfactant, all were found to possess poor early decap times, and throw distances of only 2 to 4 mm (Examples 3-7).

In terms of the quantity of water-insoluble fluorosurfactant, even extremely low loadings were found to be sufficient for providing long throw distances and excellent decap behavior (Example 9, with a 0.015 wt. % loading of fluorosurfactant). Increasing the loadings of water-insoluble fluorosurfactant by about 40 to 50%, such as in Examples 1 (0.6 wt. %) and 2 (0.7 wt. %), also provided excellent decap times and improved the throw distance—although a 1.5 wt. % loading of the water-insoluble fluorosurfactant was found to be too high, and resulted in degraded decap and throw distance performance (Example 10).

Table 4. Evaluation of Inkjet Ink Examples 1-12

	Ex 1	Ex 2	Ex 3*	Ex 4*	Ex 5*	Ex 6*	Ex 7*	Ex 8*	Ex 9	Ex 10*	Ex 11	Ex 12
Dry time	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
Decap Time/ 30 sec	Good	Good	Not Good	Not Good	Not Good	Not Good	Not Good	Not Good	Good	Not Good	Good	Good
Decap Time/ 1 min	Good	Good	Not Good	Not Good	Not Good	Not Good	Good	Not Good	Good	Not Good	Acceptable	Good
Decap Time/ 10 min	Good	Good	Good	Good	Not Good	Not Good	Good	Not Good	Good	Good	Acceptable	Good
Throw distance 2 mm	Good	Good	Good	Good	Good	Good	Good	Not Good	Good	Good	Good	Good
Throw distance 4 mm	Good	Good	Not Good	Not Good	Not Good	Not Good	Acceptable	Not Good	Good	Acceptable	Good	Good
Throw distance 6 mm	Good	Good	Not Good	Not Good	Not Good	Not Good	Not Good	Not Good	Acceptable	Not Good	Good	Good
Throw distance 8 mm	Good	Good	Not Good	Not Good	Not Good	Not Good	Not Good	Not Good	Acceptable	Not Good	Good	Good
Throw distance 10 mm	Acceptable	Acceptable	Not Good	Not Good	Not Good	Not Good	Not Good	Not Good	Acceptable	Not Good	Acceptable	Acceptable

Also as seen in Table 4, high performing inks were obtained using either a terpene resin (Examples 1, 2, 9, and 12) or terpene phenol resin (Example 11). Further, inks formulated without rosin resin (Example 12) maintained their excellent performance in all tested categories (dry time, decap time, and throw distance).

Where a numerical limit or range is stated herein, the endpoints are included. Also, all values and subranges within a numerical limit or range are specifically included as if explicitly written out.

As used herein the words "a" and "an" and the like carry the meaning of "one or more."

The present disclosure also contemplates other embodiments "comprising", "consisting of" and "consisting essentially of", the embodiments or elements presented herein, whether explicitly set forth or not.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

All patents and other references mentioned above are incorporated in full herein by this reference, the same as if set forth at length.

CLAIMS

1. An inkjet ink, comprising:

(A) a resin, which is (A1) a terpene resin or (A2) a terpene phenol resin;

(B) a solvent system comprising (B1) a ketone solvent having a boiling point of less than 120 °C; and

(C) a fluorosurfactant having a solubility in water at 25 °C of less than 0.1 wt. %.

2. The inkjet ink of claim 1, wherein the resin (A) is present in an amount of 0.1 to 10 wt. %, based on a total weight of the inkjet ink.

3. The inkjet ink of claim 1, wherein the resin (A) is the terpene resin (A1).

4. The inkjet ink of claim 3, wherein the terpene resin (A1) is a homopolymer made from α-pinene.

5. The inkjet ink of claim 1, wherein the resin (A) is the terpene phenol resin (A2).

6. The inkjet ink of claim 1, wherein the ketone solvent (B1) is present in an amount of 50 to 90 wt. %, based on a total weight of the inkjet ink.

7. The inkjet ink of claim 1, wherein a weight ratio of the ketone solvent (B1) to the resin (A) ((B1):(A)) is 10:1 to 100:1.

8. The inkjet ink of claim 1, wherein the ketone solvent (B1) is methyl ethyl ketone.

9. The inkjet ink of claim 1, wherein the solvent system (B) further comprises (B2) a glycol ether.

10. The inkjet ink of claim 9, wherein the glycol ether (B2) is present in an amount of 1 to 40 wt. %, based on a total weight of the inkjet ink.

11. The inkjet ink of claim 1, which is substantially free of solvents having a boiling point higher than 150 °C.

12. The inkjet ink of claim 1, wherein the fluorosurfactant (C) is present in an amount of from 0.001 to less than 1.5 wt. %, based on a total weight of the inkjet ink.

13. The inkjet ink of claim 1, wherein the fluorosurfactant (C) is a partially fluorinated polymeric surfactant.

14. The inkjet ink of claim 1, wherein the fluorosurfactant (C) is a partially fluorinated non-ionic polymeric surfactant.

15. The inkjet ink of claim 1, wherein the fluorosurfactant (C) is a partially fluorinated non-ionic acrylic copolymer.

16. The inkjet ink of claim 1, further comprising (D) a rosin resin.

17. The inkjet ink of claim 16, wherein the rosin resin (D) is present in an amount of 0.1 to 10 wt. %, based on a total weight of the inkjet ink.

18. The inkjet ink of claim 16, wherein the rosin resin (D) is a hydrogenated acidic rosin.

19. The inkjet ink of claim 1, further comprising (E) a colorant.

20. A printed article, comprising:

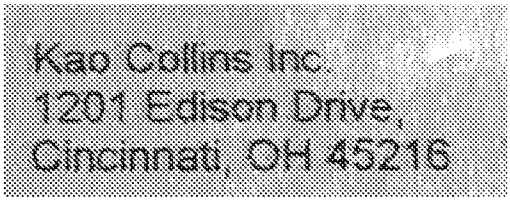
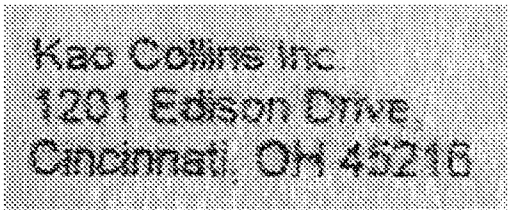
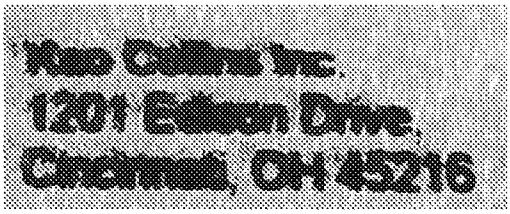
a substrate and a dried form of the inkjet ink of claim 1 disposed on the substrate.

21. A method of forming a printed image on a substrate, comprising:

applying the inkjet ink of claim 1 onto the substrate with a thermal inkjet printhead; and

drying the inkjet ink.

22. The method of claim 21, wherein the inkjet ink is dried by leaving exposed to air for 30 seconds or less without employing a heater.

Alphanumeric sequence	
	Good; clearly readable; clear image; well-defined
	Acceptable; readable; mostly clear with some haziness; slight loss of definition
	Not Good; not readable; lacks clarity; poorly defined edges

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/25055

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B41J 2/01 (2021.01)

CPC - B41J 2/01; B41J 2/04526; B41J 2/04571; C09D 11/30

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO 2020/223533 A1 (Videojet Technologies Inc.) 5 November 2020 (05.11.2020), abstract, Table 3, para[0068]-para[0069], para[0009], para[0058], para[0051], para[0040], para[0032], para[0076], para[0085], para[0043], para[0016]	1-2, 5-17, 19-22 ---------- 3-4, 18
Y	US 2014/0349037 A1 (DIC Corporation) 27 November 2014 (27.11.2014), entire document especially abstract, para[0102]	3-4
Y	US 9,051,487 B2 (OCE-Technologies B.V.) 9 June 2015 (09.06.2015), entire document especially abstract, Tabie 1	18
A	US 2019/0134989 A1 (Kao Corporation) 9 May 2019 (09.05.2019), entire document	1-22
A	US 2012/0056929 A1 (Sao et al.) 8 March 2012 (08.03.2012), entire document	1-22
A	US 2005/0134664 A1 (Pavlin) 23 June 2005 (23.06.2005), entire document	1-22
A	WO 2011/011359 A1 (Markem-Imaje Corporation) 27 January 2011 (27.01.2011), entire document	1-22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 2021	JUL 07 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300