



(43) International Publication Date
15 December 2016 (15.12.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/197234 A1

(51) International Patent Classification:

C07C 211/65 (2006.01) *C09D 11/52* (2014.01)
C01G 3/00 (2006.01) *H05K 1/03* (2006.01)
C07D 211/12 (2006.01) *H05K 1/09* (2006.01)
C07D 213/16 (2006.01) *H05K 3/12* (2006.01)

(21) International Application Number:

PCT/CA2016/050091

(22) International Filing Date:

2 February 2016 (02.02.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/174,426 11 June 2015 (11.06.2015) US

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

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

Published:

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

(54) Title: PREPARATION OF HIGH CONDUCTIVITY COPPER FILMS

(57) Abstract: A copper precursor composition contains: a first copper complex of an imine or a first cyclic amine coordinated to a first copper precursor compound; and, a second copper complex of a primary amine or a second cyclic amine coordinated to a second copper precursor compound. A copper precursor composition contains a copper complex of an imine coordinated to a copper precursor compound. The copper precursor composition is thermally degradable at a temperature lower than a comparable composition containing only primary amine copper complexes under otherwise the same conditions to produce a metallic copper film having a resistivity of about 200 $\mu\Omega$ -cm or less. Inks containing the copper precursor composition and a solvent may be deposited on a substrate and sintered to produce a metallic copper film. The substrate with the film thereon is useful in electronic devices.



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PREPARATION OF HIGH CONDUCTIVITY COPPER FILMS

Cross-reference to Related Applications

This application claims the benefit of United States Provisional Patent Applications
USSN 62/174,426 filed June 11, 2015, the entire contents of which is herein incorporated
5 by reference.

Field

This application relates to processes and compositions for preparing high
conductivity copper films on substrates, especially for use in flexible circuits.

Background

10 The production of low cost electronics relies on the ability to print conductive
circuits using additive printing techniques on inexpensive plastic substrates. Formulating
conductive inks that function with low cost printing techniques, such as inkjet, screen,
flexo or gravure printing, while providing the required electrical and mechanical
performance is still a challenge in printable electronics as smaller dimensions and high
15 density will enable new applications. Although flake-based silver conductive inks meet
many of today's requirements and silver nanoparticles inks have promise due to their
excellent electrical properties, few options exist for cost effective inks based on copper
despite their superiority with regards to electromigration, which plagues silver circuits and
will become increasingly important as higher density designs become implemented.

20 Thermal decomposition of anhydrous copper (II) formate ($\text{Cu}(\text{OOCH})_2$) has been
shown to occur near 200°C yielding Cu^0 , H_2 and CO_2 in a stepwise cation reduction
reaction with copper (I) formate as an intermediate. Copper coordination compounds are
compelling ink materials as they are inexpensive, easy to prepare and process,
compatible with a range of different printing methods and have excellent electrical
25 performance. For instance, copper (II) formate coordinated to alkylamines, such as
hexylamine and octylamine, convert to metallic copper by thermal decomposition under
relatively mild conditions providing metallic copper traces with resistivity values as low as
5.0 $\mu\Omega\cdot\text{cm}$. Unfortunately, the sintering conditions typically used all cause polyethylene
terephthalate (PET) to deform, especially under tension, thereby limiting their use. In
30 addition, the sintering times on the order of 30 min lessens their appeal in a roll-to-roll
process. PET is an inexpensive substrate desirable for the fabrication of low cost
electronics using with screen or inkjet printing.

Copper formates coordinated with pyridine derivatives have been used as precursors for metallic copper (US 6,770,122). Copper formates coordinated with piperidine derivatives have been used as precursors for metallic copper (US 2014/0349017). However, these documents do not demonstrate utility to make printable inks that can also be sintered at low temperatures, in less time and at ambient pressure compatible with PET to produce copper films of low resistivity.

Summary

There is provided a copper precursor composition comprising: a first copper complex comprising an imine or a first cyclic amine coordinated to a first copper precursor compound; and, a second copper complex comprising a primary amine or a second cyclic amine coordinated to a second copper precursor compound, the copper precursor composition thermally degradable at a temperature lower than a comparable composition comprising only the second copper complex under otherwise the same conditions to produce a metallic copper film having a resistivity of about $200 \mu\Omega \cdot \text{cm}$ or less.

There is further provided a copper precursor composition comprising a copper complex comprising an imine coordinated to a copper precursor compound.

There is further provided a copper ink comprising a copper precursor composition as described above and a solvent.

There is further provided a substrate comprising a trace of the copper ink deposited on a surface of the substrate.

There is further provided a process for producing a metallic copper film comprising: depositing the copper ink on a surface of a substrate; and, sintering the ink to produce a metallic copper film.

Further features will be described or will become apparent in the course of the following detailed description. It should be understood that each feature described herein may be utilized in any combination with any one or more of the other described features, and that each feature does not necessarily rely on the presence of another feature except where evident to one of skill in the art.

Brief Description of the Drawings

For clearer understanding, preferred embodiments will now be described in detail by way of example, with reference to the accompanying drawings, in which:

Fig. 1A depicts a graph showing resistivity ($\mu\Omega\cdot\text{cm}$) as a function of the weight fraction of 3ButPy to EtHex after heating to 170°C.

Fig. 1B depicts a graph showing resistivity ($\mu\Omega\cdot\text{cm}$) of copper films made from EtHex (black diamond) and a blend of 60% 3ButPy (white square) as a function of
5 sintering temperature.

Fig. 2 depicts a graph showing resistivity ($\mu\Omega\cdot\text{cm}$) of copper films made from various DiMetPip inks and sintered between 110°C and 150°C.

Fig. 3A depicts a graph showing TGA of copper (II) formate coordinated to various amines.

10 Fig. 3B depicts a graph showing DTGA of copper (II) formate coordinated to various amines.

Detailed Description

In one embodiment, the copper precursor composition comprises a first copper complex comprising an imine or a first cyclic amine coordinated to a first copper precursor
15 compound, and a second copper complex comprising a primary amine or a second cyclic amine coordinated to a second copper precursor compound. Preferably, the first copper complex comprises: two cyclic amines, which may be the same or different, preferably the same; two imines, which may be the same or different, preferably the same; or, one cyclic amine and one imine. Preferably, the second copper complex comprises: two primary
20 amines, which may be the same or different, preferably the same; two cyclic amines, which may be the same or different, preferably the same; or, one primary amine and one cyclic amine. The first and second copper complexes are different complexes.

In another embodiment, the copper precursor composition comprises a copper complex comprising an imine coordinated to a copper precursor compound.

25 Cyclic amines comprise a ring structure comprising one or more nitrogen atoms in the ring. The ring may contain, for example, 1, 2 or 3 nitrogen atoms. At least one of the nitrogen atoms should be available for coordination to copper. Preferably, the ring contains 1 or 2 nitrogen atoms, more preferably 1 nitrogen atom. The ring also contains at least one carbon atom, preferably 1-7 carbon atoms. The ring may also contain one or
30 more heteroatoms, for example O or S. Preferably, the ring comprises only nitrogen and carbon atoms. Preferably, the cyclic amine comprises a 4-membered ring, a 5-membered ring, a 6-membered ring, a 7-membered ring or an 8-membered ring. 5-membered rings,

6-membered rings and 7-membered rings are especially preferred. 6-membered rings are most preferred. The cyclic amine may comprise one or more ring structures, where the ring structures are fused or unfused. At least one of the ring structures contains a nitrogen atom, whereas the other ring structures may or may not contain a nitrogen atom.

5 The ring structures may be aromatic or non-aromatic.

The rings may be unsubstituted or substituted with one or more substituents. Substituents may include, for example, hydrogen, halogen, hydroxyl, sulfhydryl, carboxyl, substituted carboxyl, alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl and substituted alkynyl. Substituted substituents may be substituted with one or substituents,
10 which may be the same as those listed above. Preferably, the substituents comprise alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl or substituted alkynyl. Substituents on the rings are preferred in some embodiments because substituents on the rings may help the first copper complex be more compatible with the second copper complex. In this regard, the substituents on the rings of the first copper complex
15 preferably have similar solubility properties as the organic groups that form part of the primary amines or cyclic amines of the second copper complex. Compatibilization of the first and second copper complexes may reduce a tendency for one or the other of the copper complexes to crystallize.

The cyclic amine preferably comprises from 1 to 30 carbon atoms and from 1 to 3
20 nitrogen atoms. The cyclic amine more preferably comprises from 4 to 20 carbon atoms. The cyclic amine more preferably comprises 1 nitrogen atom, which is in the ring structure and available for coordination to the copper of the first copper precursor compound. Preferably, the ring structure in the cyclic amine comprises from 4 to 6 carbon atoms. Any substituents on the ring structure preferably each comprise from 1 to 8 carbon
25 atoms. Preferably, the ring structures comprise from 1 to 3 substituents other than hydrogen. Preferably there is 1 ring structure in the cyclic amine.

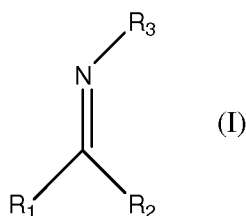
Some examples of nitrogen-containing ring structures include unsubstituted or substituted aziridine, diazine, azetidine, dihydroazete, diazetidine, pyrrolidine, pyrrole, imidazolidine, pyrazolidine, imidazole, pyrazoline, pyrazole, triazole, tetrazole, piperidine,
30 pyridine, tetrahydropyran, pyran, piperazine, pyrazine, pyrimidine, pyridazine, morpholine, triazine, azepane, azepine, homopiperazine, diazepine, azocane, azocine and structural isomers thereof. Pyridine and piperidine are particularly preferred.

Other than hydrogen, substituents on the ring structures preferably include C₁₋₈ alkyl groups, C₂₋₈ alkenyl groups and C₂₋₈ alkynyl groups. C₁₋₈ alkyl groups are more

preferred. C₁₋₈ alkyl groups include, for example, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *sec*-butyl, *tert*-butyl, pentyl, hexyl, heptyl, octyl and isomers thereof.

Of particular note are alkyl-substituted pyridines and piperidines. One or more alkyl groups may be substituted on the pyridine or piperidine ring. Preferably, there are
 5 from 1 to 3 alkyl substituents, more preferably 1 or 2 alkyl substituents. The alkyl substituents are preferably C₁₋₈ alkyl groups.

Imines contain at least one nitrogen atom that coordinates to copper. Imines of Formula (I) are preferred:



10 where R₁, R₂ and R₃ are the same or different and may be H, alkyl (e.g. C₁₋₈ alkyl), alkenyl (e.g. C₂₋₈ alkenyl), alkynyl (e.g. C₂₋₈ alkynyl), cycloalkyl (e.g. C₃₋₈ cycloalkyl), aryl (e.g. C₆₋₁₄ aryl), alkaryl (e.g. C₇₋₂₀ alkaryl), aralkyl (e.g. C₇₋₂₀ aralkyl), OH, O-alkyl (e.g. O-C₁₋₈ alkyl), O-aralkyl (e.g. O-C₇₋₂₀ aralkyl), O-alkaryl (e.g. O-C₇₋₂₀ alkaryl), CO₂-alkyl (e.g. CO₂-(C₁₋₈ alkyl)), SO₂-alkyl (e.g. SO₂-(C₁₋₈ alkyl)) or SO-alkyl (e.g. SO-(C₁₋₈ alkyl)) or R₁ and R₂
 15 taken together form a ring (e.g. a C₃₋₈ ring), with the proviso that at least one of R₁, R₂ and R₃ is not H.

In R₁, R₂ and R₃, alkyl groups include, for example, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *sec*-butyl, *tert*-butyl, pentyl, hexyl, heptyl, octyl and isomers thereof. Aryl groups include, for example, phenyl, naphthyl and anthracyl. Cycloalkyl groups include,
 20 for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. Aralkyl groups include, for example (C₆₋₁₄ aryl)(C₁₋₄ alkyl)_x, where x is 1-3. Alkaryl groups include, for example, (C₁₋₄ alkyl)(C₆₋₁₄ aryl).

Cyclic imines are of particular note. Some examples of cyclic imines are unsubstituted and substituted azirine, azete and pyrroline.

25 Primary amines of the formula R-NH₂ are preferred, where R is an organic group. R is preferably a C₃-C₂₀ organic group, more preferably a C₆-C₁₂ organic group. The organic group is preferably an unsubstituted alkyl group, an unsubstituted alkenyl group or an unsubstituted alkynyl group, more preferably an unsubstituted alkyl group. The

unsubstituted alkyl, alkenyl or alkynyl groups are preferably straight or branched chains. Some particular examples of primary amines include hexylamine, octylamine and ethylhexylamine.

Copper precursor compounds comprise a copper ion, preferably a copper (II) ion, and one or more ligands coordinated to the copper ion. The one or more ligands may be any ligand which is removable from the copper ion by the action of heat. Suitable ligands for copper precursor compounds are known in the art. Some examples of suitable ligands include organic or inorganic ligands that bind to the copper through an atom other than carbon such as oxygen, nitrogen, sulfur and halogen. A combination comprising at least one of the foregoing can be used. Inorganic ligands include, for example, nitrate, carbonate, halide, perchlorate, hydroxide and tetrafluoroborate. Organic ligands include, for example, carboxylates, sulfonates and amides. Preferably, there are two ligands coordinated to the copper precursor compounds. The two ligands may be the same or different, preferably the same. The one or more ligands preferably comprise carboxylate anions, for example, formate, acetate, oxalate, propionate, butanoate, ethylhexanoate, neodecanoate, pentafluoropropionate, citrate, glycolate, benzoate, trifluoroacetate, phenylacetate, acetylacetonate and hexafluoroacetyl-acetonate groups. C₁₋₁₂ alkanoates are particularly preferred. Formate is most preferred. The first and second copper precursor compounds may be the same or different, preferably the same.

Copper complexes may be prepared by reacting cyclic amine, imine or primary amine, as the case may be, with the copper precursor compound. The copper precursor compound may comprise one or more coordinated leaving groups (e.g. water, ammonia and the like), which are displaced by the cyclic amine, imine or primary amine during the reaction. The reaction may be conducted in a solvent, preferably a solvent that facilitates the displacement of the leaving group while not out-competing the cyclic amine, imine or primary amine for coordination to the copper. Such solvents are well known in the art, for example acetonitrile, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and the like. In some cases the reaction may be performed at elevated temperatures to assist in the displacement of the leaving group. The amount of cyclic amine, imine or primary amine depends on the number of such molecules to be coordinated to the copper. Using two molar equivalents of cyclic amine, imine or primary amine with one molar equivalent of copper precursor compound permits coordination of two molecules of the cyclic amine, imine or primary amine to the copper.

The amount of the first copper complex and second copper complex in a copper precursor composition may be adjusted by simple experimentation to determine the best

ratio of one to the other depending on the nature of the first and second copper complexes. The amount (w/w) of the first copper complex with respect to the second copper complex may be in the range of about 1-99% based on total weight of the first and second copper complexes, preferably about 5-95%, more preferably about 10-75%, or
5 about 20-75%, or about 40-75%, or about 50-75%, or about 60-66%.

The copper ink comprises a solvent in addition to the copper precursor composition. The copper precursor composition may comprise about 1-99 wt% of the ink, based on weight of the ink. Preferably, the copper precursor composition comprises about 5-95 wt%, or about 10-90 wt%, or about 20-80 wt% of the ink. The solvent
10 generally makes up the balance of the ink after considering all other components including the copper precursor composition, any binders that are present and any other component. The balance may be, in some instances, about 1-99 wt%, based on weight of the ink. The solvent preferably comprises about 5-95 wt%, or about 15-95 wt%, or about 20-75 wt%, or about 20-40 wt% of the ink.

15 The solvent may comprise an aqueous medium, an organic medium or a mixture thereof. Aqueous media comprise water or water with one or more other ingredients dispersed therein. Organic media may comprise an organic solvent or mixture of organic solvents. The copper precursor composition is preferably dispersable, more preferably soluble, in the solvent.

20 Organic solvents include, for example, alcohol-based solvents, diol-based solvents, ketone-based solvents, ester-based solvents, ether-based solvents, aliphatic or alicyclic hydrocarbon-based solvents, aromatic hydrocarbon-based solvents, cyano-containing hydrocarbon solvents, and other solvents.

Alcohol-based solvents include, for example, methanol, ethanol, propanol, isopropanol, 1-butanol, isobutanol, 2-butanol, tertiary butanol, pentanol, isopentanol, 2-pentanol, neopentanol, tertiary pentanol, hexanol, 2-hexanol, heptanol, 2-heptanol, octanol, 2-ethylhexanol, 2-octanol, cyclopentanol, cyclohexanol, cycloheptanol, methylcyclopentanol, methylcyclohexanol, methylcycloheptanol, benzyl alcohol, ethylene glycol monoacetate, ethylene glycol monoethyl ether, ethylene glycol monophenyl ether,
25 ethylene glycol monobutyl ether, ethylene glycol monomethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monobutyl ether, 2-(2-methoxyethoxy)ethanol, 2-(N,N-dimethylamino)ethanol, 3-(N,N-dimethylamino)propanol, and the like.
30

Diol-based solvents include, for example, ethylene glycol, propylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, isoprene glycol (3-methyl-1,3-butanediol), 1,2-hexanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,2-octanediol, octanediol (2-ethyl-1,3-hexanediol), 2-butyl-2-ethyl-1,3-
 5 propanediol, 2,5-dimethyl-2,5-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and the like.

Ketone-based solvents include, for example, acetone, ethyl methyl ketone, methyl butyl ketone, methyl isobutyl ketone, ethyl butyl ketone, dipropyl ketone, diisobutyl ketone, methyl amyl ketone, cyclohexanone, methylcyclohexanone, and the like.

10 Ester-based solvents include, for example, methylformate, ethyl formate, methyl acetate, ethyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, sec-butyl acetate, *tert*-butyl acetate, amyl acetate, isoamyl acetate, *tert*-amyl acetate, phenyl acetate, methyl propionate, ethyl propionate, isopropyl propionate, butyl propionate, isobutyl propionate, sec-butyl propionate, *tert*-butyl propionate, amyl propionate, isoamyl
 15 propionate, *tert*-amyl propionate, phenyl propionate, methyl 2-ethylhexanoate, ethyl 2-ethylhexanoate, propyl 2-ethylhexanoate, isopropyl 2-ethylhexanoate, butyl 2-ethylhexanoate, methyl lactate, ethyl lactate, methyl methoxypropionate, methyl ethoxypropionate, ethyl methoxypropionate, ethyl ethoxypropionate, ethylene glycol monomethyl ether acetate, dichthylen glycol monomethyl ether acetate, ethylene glycol
 20 monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monoisopropyl ether acetate, ethylene glycol monobutyl ether acetate, ethylene glycol mono-sec-butyl ether acetate, ethylene glycol monoisobutyl ether acetate, ethylene glycol mono-*tert*-butyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, propylene
 25 glycol monoisopropyl ether acetate, propylene glycol monobutyl ether acetate, propylene glycol mono-sec-butyl ether acetate, propylene glycol monoisobutyl ether acetate, propylene glycol mono-*tert*-butyl ether acetate, butylene glycol monomethyl ether acetate, butylene glycol monoethyl ether acetate, butylene glycol monopropyl ether acetate, butylene glycol monoisopropyl ether acetate, butylene glycol monobutyl ether acetate,
 30 butylene glycol mono-sec-butyl ether acetate, butylene glycol monoisobutyl ether acetate, butylene glycol mono-*tert*-butyl ether acetate, methyl acetoacetate, ethyl acetoacetate, methyl oxobutanoate, ethyl oxobutanoate, γ -lactone, α -lactone, and the like.

Ether-based solvents include, for example, tetrahydrofuran, tetrahydropyran, morpholine, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene
 35 glycol dimethyl ether, dibutyl ether, diethyl ether, dioxane, and the like.

Aliphatic or alicyclic hydrocarbon solvents include, for example, pentane, hexane, cyclohexane, methylcyclohexane, dimethylcyclohexane, ethylcyclohexane, heptane, octane, decaline, solvent naphtha, and the like.

Aromatic hydrocarbon-based solvents include, for example, benzene, toluene, 5 ethylbenzene, xylene, trimethylbenzenes (e.g. mesitylene), diethylbenzene, cumene, isobutylbenzene, cymene, tetralin, chlorobenzene, benzyl ether, anisole, benzonitrile, propylbenzene, cumene, isobutylbenzene, indane, tetralin, durene, indane, and the like.

Cyano-containing hydrocarbon solvents include, for example, include 1- 10 cyanopropane, 1-cyano butane, 1-cyano hexane, cyanocyclohexane, cyanobenzene, 1,3-dicyanopropane, 1,4-dicyanobutane, 1,6-dicyano hexane, 1,4-dicyanocyclohexane, 1,4-dicyanobenzene, and the like.

In some embodiments, the solvent may be the same as the amines or imines used to form the copper complexes.

The copper ink may also comprise a binder. A binder is any material that binds the 15 ink together into a film and binds the ink to a surface on which the ink is deposited. The binder preferably comprises a polymeric material, especially an organic polymer. The amount of binder may be expressed in terms of the total mass of the copper in the copper precursor composition. Preferably, the binder may be present in the ink in a range of about 2.5-55 wt% based on weight of the copper in the copper precursor composition. 20 Weight of the copper in the copper precursor composition is the total weight of the copper without the other elements that comprise the precursor composition. More preferably, the binder is in a range of about 5-35 wt% based on weight of the copper in the copper precursor composition. The binder preferably comprises an organic polymeric binder, for example, ethyl cellulose, polypyrrolidone, epoxies, phenolic resins, phenol formaldehyde 25 resins (e.g. Novolac™, Resole™), acrylics, urethanes, silicones, styrene allyl alcohols, polyalkylene carbonates, polyvinyl acetals, polyesters, polyurethanes, polyolefins, fluoroplastics, fluoroelastomers, thermoplastic elastomers or any mixture thereof.

The substrate may be any surface on to which the ink may be deposited, preferably any printable surface. Surfaces may comprise, for example, polyethylene 30 terephthalate (PET), polyolefin (e.g. silica-filled polyolefin (Teslin™)), polyethylene naphthalate (PEN), polydimethylsiloxane (PDMS), polystyrene, polycarbonate (PC), polyimide (e.g. Kapton™), silicone membranes, epoxy resin (e.g. glass-reinforced epoxy resin laminate), textiles (e.g. cellulosic textiles), paper, glass, metal, dielectric coatings,

among others. Plastic substrates are preferred. Flexible substrates are preferred. Polyethylene terephthalate, polyethylene naphthalate, polycarbonate and FR-4 (glass-reinforced epoxy resin laminate) are preferred, especially polyethylene terephthalate, polyethylene naphthalate and FR-4. Polyethylene terephthalate (PET) is of particular
5 note.

Inks may be deposited on a substrate by any suitable method, for example screen printing, inkjet printing, flexography printing (e.g. stamps), gravure printing, off-set printing, airbrushing, aerosol printing, typesetting, spin coating, dip coating spray coating, roll coating, knife coating, bar coating, slit coating, brush coating or any other method.
10 Printing methods are preferred. After deposition, the ink may be dried or cured, for example by allowing the ink to dry in ambient conditions or heating the ink for an appropriately long period of time to evaporate the solvent. The inks of the present invention are particularly suited to inkjet, screen, roll-to-roll, flexography or gravure printing. The inks are well-suited for roll-to-roll printing as they require lower temperature
15 and less time to sinter.

The ink may be deposited, for example printed, onto a substrate to form a trace of the ink on the substrate. Drying and decomposing the trace to form conductive copper films may be accomplished by any suitable technique, where the techniques and conditions are guided by the type of substrate on which the ink traces are deposited.
20 Heating the substrate dries and sinters the trace to form a conductive copper film. Sintering decomposes the copper precursor composition to form conductive copper nanoparticles. Heating is preferably performed at a temperature of about 150°C or less, or about 140°C or less, or about 135°C or less, or about 130°C or less, or about 125°C or less. Heating is preferably performed at a temperature of about 90°C or more, or about
25 100°C or more. The ink trace is preferably sintered for a time of about 30 min or less, or about 10 min or less, or about 5 min or less. There is a balance between temperature and time whereby sintering at lower temperature generally requires a longer time. Pressure may also be adjusted during sintering to alter the temperature and/or time required to form conductive copper films. The pressure is preferably about 3 atm or less, or about 2
30 atm or less. In one embodiment, no additional pressure is used. The type of heating apparatus also factors into the temperature and time required for sintering. Sintering may be performed with the substrate under an oxidizing atmosphere (e.g. air) or an inert atmosphere (e.g. nitrogen and/or argon gas). For copper inks, an inert or a reducing atmosphere may be desired, or an oxygen depleted atmosphere having an oxygen
35 content of preferably about 1000 ppm or less, more preferably about 500 ppm or less.

Sintering conditions (time, temperature and pressure) required for inks of the present invention may be amenable to roll-to-roll printing, a feature that was previously not possible with the primary amine coordinated copper formate complexes due to relatively long sintering times. Further, sintering conditions may be amenable for printing
5 on PET substrates, another feature that was previously not possible with the primary amine coordinated copper formate complexes. Copper precursor compositions of the present invention reduce the temperature at which the ink needs to be sintered to produce copper films of good conductivity (low resistivity) in a short period of time.

A conductive copper film produced from the copper precursor composition
10 preferably has a resistivity of about $150\ \mu\Omega\cdot\text{cm}$ or less, or about $100\ \mu\Omega\cdot\text{cm}$ or less, or even as low as $50\ \mu\Omega\cdot\text{cm}$ or less. Conductive copper films may have resistivity values at least as good as currently known inks, while being produced at lower sintering temperatures in less time.

The substrate may be incorporated into an electronic device, for example
15 electrical circuits, conductive bus bars (e.g. for photovoltaic cells), sensors, antennae (e.g. RFID antennae), touch sensors, thin film transistors and smart packaging (e.g. smart drug packaging). The substrates may be used as any conductive element, for example interconnectors. The copper precursor composition and inks produced therefrom enable miniaturization of such electronic devices.

20 EXAMPLES:

Example 1: Synthesis of amine copper (II) formate complexes

Copper (II) formate complexes are prepared by coordinating 2 molar equivalents of different amines with 1 molar equivalent of copper (II) formate.

Bis(2-ethyl-1-hexylamine) copper (II) formate (EtHex) was prepared by
25 suspending 1.0 g of copper (II) formate dihydrate in 25 mL of acetonitrile and adding 1.74 mL of 2-ethyl-1-hexylamine (a primary amine). The solution was immediately filtered to remove unreacted copper (II) formate and subsequently rotary evaporated to remove the acetonitrile.

Bis(3-butylpyridine) copper (II) formate (3ButPy) was prepared in a similar manner
30 as primary amine copper (II) formate complexes by suspending 1.0 g of copper (II) formate dihydrate in 25 mL of acetonitrile and adding 1.57 mL of 3-butylpyridine (a

pyridine). The solution was immediately filtered to remove unreacted copper formate and subsequently rotary evaporated to remove the acetonitrile.

Bis(3,5-dimethylpiperidine) copper (II) formate (DiMePip) was prepared by suspending 2 g of copper (II) formate dihydrate in 50 mL of acetonitrile and adding 2.809
5 mL of 3,5-dimethylpiperidine (a piperidine). The solution was immediately filtered to remove unreacted copper (II) formate and subsequently rotary evaporated to remove the acetonitrile.

Bis(octylamine) copper (II) formate (Octyl) and bis(4-*t*-butylpyridine) copper (II) formate (*t*ButPy) complexes were prepared in a similar manner as described above.

10 *Example 2: Preparation of copper precursor compositions and copper inks*

Inks of individual amine copper (II) formate complexes were prepared by mixing 1.00 g of the complex with 20%-40% (g/g) of anisole. The mixtures were homogenized by planetary mixing for 8 minutes.

Copper precursor compositions comprising a primary amine copper (II) formate
15 complex and either a pyridine copper (II) formate complex or a piperidine copper (II) formate complex were prepared by mixing a primary amine copper (II) formate complex with either a pyridine copper (II) formate complexes or a piperidine copper (II) formate complex. The mixtures varied from 25% to 80% (g/g) of the primary amine copper (II) formate complex. Inks of the copper precursor compositions were prepared by mixing
20 1.00 g of the copper precursor compositions, containing the desired mixture of primary amine copper (II) formate complex and pyridine or piperidine copper (II) formate complex, with 20%-40% (g/g) of anisole. The mixtures of the copper precursor compositions and anisole were homogenized by planetary mixing for 8 minutes.

Example 3: Formation of copper films on substrates

25 Inks prepared above were printed on Kapton™ substrates (polyimide) as squares with dimensions of 1 cm x 1 cm. For inks containing pyridine copper (II) formate complexes, the inks were heated through convection using a Kar-X-Reflow 306 LF convection oven in a nitrogen atmosphere with an oxygen concentration below 200 ppm, in which the squares were heated at a temperature of 135°C to 185°C for 5 minutes. For
30 inks containing piperidine copper (II) formate complexes, the inks were heated through conduction using a hotplate in a nitrogen glove box with an oxygen concentration below 1.0 ppm, where the squares were heated at a temperature of 110°C to 150°C for 5

minutes. For comparison, inks containing only primary amine copper (II) formate complexes were heated by both methods. Heating the inks on the substrate resulted in the formation of copper films on the substrates.

Inks comprising the alkylamine complexes, or mixtures of the alkylamine complexes and the pyridine or piperidine complexes, decomposed into films without significant cracking. However, inks comprising only tButPy and 3ButPy decomposed into films with significant cracking. As a result, electrical resistance measurements of films produced from inks comprising only tButPy and 3ButPy were unreliable. Decreasing the rate of heating and lowering the sintering temperatures did not improved the film quality for films produced from inks comprising only tButPy and 3ButPy. Inks containing a mixture of EtHex and 3ButPy combined the good film forming properties of EtHex and the low decomposition temperature of 3ButPy.

Example 4: Resistivity of copper traces

Resistivity values of the copper films were determined on the 1 cm x 1 cm squares using a four-point probe technique. A Keithley 220 programmable current source, a HP 3478A multimeter and a SP4 tip from Lucas Lab were used for the four-point probe measurement.

The optimal weight fraction of 3ButPy (e.g. 3ButPy/[3ButPy+EtHex]) was determined at about 170°C to ensure that all blend variants were fully sintered. Fig. 1A shows that the resistivity of the films gradually decreases as the fraction of 3ButPy increases. A minimum resistivity of 6.5 $\mu\Omega\cdot\text{cm}$ was achieved with 60% 3ButPy. In Fig. 1B, the resistivity values of pure EtHex complex (diamonds) are compared to a blend of 60% 3ButPy (squares) in order to assess their performance as a function of temperature. The resistivity trends lower as the sintering temperature is increased to 170°C in both cases but increases at 185°C concurrent with increases in the error in the resistivity values and the presence of a blackened surface. Therefore, above a sintering temperature of 170°C, oxidation plays an increasingly important role in degrading the electrical characteristics of the films. At 170°C, the 3ButPy/EtHex ink outperformed the pure EtHex ink in terms of resistivity and at 135°C produced films with a resistivity of 13.9 $\mu\Omega\cdot\text{cm}$, whereas the EtHex derived traces were non-conductive. On examining the behavior of PET substrates under these sintering conditions, it was found that PET substrates did not show signs of deformation up to a temperature of 135°C. Table 1 illustrates substrate compatibility of EtHex and 3ButPy/EtHex inks based on resistivity values obtained by sintering 5 min at

various temperatures. Table 2 illustrates the sheet resistances of copper films formed from the EtHex and 3ButPy/EtHex inks at various sintering temperatures.

Table 1

Ink	Sintering T (°C)	Resistivity ($\mu\Omega\cdot\text{cm}$)	Substrate Compatibility
EtHex	135	non-conductive	none
	170	12.3	PEN, Kapton™
3ButPy/EtHex (60% 3ButPy)	135	13.9	PET
	170	6.5	PEN, Kapton™

5

Table 2

Ink	Sintering T (°C)	Sheet Resistance (Ω/\square)	Standard Error	Film Thickness (nm)
EtHex	135			
	155	0.438	0.05	2800
	170	0.226	0.023	4600
	185	0.75	0.24	2900
3ButPy/EtHex	135	0.346	0.031	4000
	155	0.261	0.013	4300
	170	0.760	0.057	5150
	185	0.209	0.048	6100

Table 3 illustrates sheet resistances (Ω/\square) for copper films produced from 3ButPy/EtHex inks of varying compositions when sintered at 170°C.

Table 3

3ButPy:EtHex	Sheet Resistance (Ω/\square)	Standard Error	Film Thickness (nm)
0	0.0338	0.0024	4110
0.2	0.0263	0.0035	4380
0.25	0.0274	0.0028	4540
0.33	0.00891	0.0011	11100
0.5	0.0095	0.0006	8580
0.6	0.0076	0.0006	8700
0.67	0.0275	0.0072	5150

10

Fig. 2 shows the resistivity of copper films made from various DiMePip-containing inks as a function of temperature. The films made from pure EtHex show the lowest

resistivity of all the ink mixtures but do not conduct when sintered at 110°C. Although the films made from pure DiMetPip show higher resistivity, DiMetPip and mixtures containing more than 50% DiMetPip conduct when sintered at 110°C. Thus, mixtures of DiMetPip and EtHex form conductive copper films when sintered at lower temperatures than EtHex alone and form copper films with better conductivity than films formed from DiMetPip alone. Inks with EtHex alone must be sintered at higher temperatures in order to form conductive copper films and DiMetPip alone results in copper films of lower conductivity (higher resistivity).

Example 5: Thermogravimetric analysis of amine copper (II) formate complexes

Amine copper (II) formate complexes underwent thermogravimetry analysis (TGA) on a Netzsch TG 209 F1 Iris R. The system was run with BOC HP argon (grade 5.3) gas and residual oxygen was trapped with a Supelco Big-Supelpure oxygen/water trap. Fig. 3A and Fig. 3B show the mass loss (TGA) and derivative of the mass loss (DTGA) of the complexes as they are heated to 400°C under Argon. The graphs show that the decomposition temperatures of the complexes decrease in the following order: primary alkylamine > secondary alkylamine > secondary cyclic alkylamine > tertiary cyclic aromatic amine.

The tButPy and 3ButPy complexes decompose between 90-130°C and 75-120°C, respectively, whereas the mass loss of Octyl and EtHex complexes spans 100-155°C. The two peaks in mass loss point to a two-step reduction of copper complex to metallic copper. The pyridine complexes decompose within a narrower temperature range than the alkylamine complexes suggesting formation of smaller copper particles with a narrower size distribution, which was confirmed by scanning electron microscope (SEM) images of the copper films. tButPy leads to copper particles having smaller diameters and narrower size distributions (26 ± 6 nm) than particles made from EtHex (100 ± 30 nm) and Octyl (240 ± 60 nm).

Pyridine and piperidine derivatives coordinated to copper (II) formate have lower decomposition temperatures than the alkylamine counterparts. The 3-butyl-pyridine ligand, coordinated to copper (II) formate, initiates decomposition near 80°C, 30°C lower than alkylamine-Cu(OOCH)₂ derivatives. Although on its own bis(3-butyl-pyridine) copper (II) formate has poor film forming properties, the complex can be combined with bis(2-ethyl-1-hexylamine) copper (II) formate to yield an ink with good film forming properties, short sintering times and low decomposition temperatures. Inks that combine pyridine-Cu(OOCH)₂ or piperidine-Cu(OOCH)₂ with alkylamine-Cu(OOCH)₂ generate copper films

with high conductivity values (low resistivity values) while being produced in a lower temperature process.

References: The contents of the entirety of each of which are incorporated by this reference.

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5 The novel features will become apparent to those of skill in the art upon examination of the description. It should be understood, however, that the scope of the claims should not be limited by the embodiments, but should be given the broadest interpretation consistent with the wording of the claims and the specification as a whole.

Claims:

1. A copper precursor composition comprising:

a first copper complex comprising an imine or a first cyclic amine coordinated to a first copper precursor compound; and,

5 a second copper complex comprising a primary amine or a second cyclic amine coordinated to a second copper precursor compound,

the copper precursor composition thermally degradable at a temperature lower than a comparable composition comprising only the second copper complex under otherwise the same conditions to produce a metallic copper film having a resistivity of
10 about 200 $\mu\Omega\cdot\text{cm}$ or less.
2. The composition according to claim 1, wherein the first copper complex comprises two imines or two cyclic amines.
3. The composition according to claim 1 or 2, wherein the first copper complex comprises a cyclic amine, and the cyclic amine comprises a 6-membered ring.
- 15 4. The composition according to claim 3, wherein the 6-membered ring is pyridine or piperidine.
5. The composition according to any one of claims 1 to 4, wherein the cyclic amine is substituted with one or more C_{1-8} alkyl groups.
6. The composition according to any one of claims 1 to 5, wherein the first copper
20 precursor compound comprises a copper (II) ion and one or more carboxylate anions coordinated to the copper (II) ion.
7. The composition according to claim 6, wherein the one or more carboxylate anions are two formate groups.
8. The composition according to any one of claims 1 to 7, wherein the second
25 copper complex comprises two primary amines.
9. The composition according to any one of claims 1 to 8, wherein the primary amine has formula R-NH_2 , where R is a $\text{C}_6\text{-C}_{12}$ unsubstituted alkyl group.

10. The composition according to any one of claims 1 to 9, wherein the primary amine is octylamine or ethylhexylamine.
11. The composition according to any one of claims 1 to 10, wherein the second copper precursor compound comprises a copper (II) ion and one or more carboxylate anions coordinated to the copper (II) ion.
12. The composition according to claim 11, wherein the one or more carboxylate anions are two formate groups.
13. The composition according to any one of claims 1 to 12, wherein the first copper complex is present in the composition in an amount of about 20-75% (w/w) based on total weight of the first and second copper complexes.
14. A copper complex comprising an imine coordinated to a copper precursor compound.
15. A copper ink comprising the copper precursor composition as defined in any one of claims 1 to 14 and a solvent.
16. The ink according to claim 1, wherein the copper precursor composition comprises 20-80 wt% of the ink based on total weight of the ink.
17. The ink according to claim 15 or 16 further comprising a binder.
18. A substrate comprising a trace of the copper ink according to any one of claims 15 to 17 deposited on a surface of the substrate.
19. The substrate according to claim 18, which comprises a flexible plastic.
20. The substrate according to claim 18 or 19, which comprises polyethylene terephthalate (PET), polyolefin, polyethylene naphthalate (PEN), polydimethylsiloxane (PDMS), polystyrene, polycarbonate, polyimide or glass-reinforced epoxy resin laminate.
21. The substrate according to claim 18, which comprises polyethylene terephthalate (PET).
22. A process for producing a metallic copper film comprising: depositing the copper ink as defined in any one of claims 15 to 17 on a surface of a substrate; and, sintering the ink to produce a metallic copper film.

23. The process according to claim 22, wherein the sintering is performed at a temperature of 150°C or less.
24. The process according to claim 23, wherein the temperature is 135°C or less.
25. The process according to claim 23, wherein the temperature is 125°C or less.
- 5 26. The process according to claim 23, wherein the temperature is in a range of 100-130°C.
27. The process according to any one of claims 22 to 26, wherein the sintering is performed for a time of 10 min or less.
28. The process according to claim 27, wherein the time is 5 min or less.
- 10 29. The process according to any one of claims 22 to 28, wherein pressure during sintering is 2 atm or less.
30. The process according to any one of claims 22 to 29, wherein the ink is deposited on the substrate by inkjet, screen, roll-to-roll, flexography or gravure printing.
31. The process according to any one of claims 22 to 30, wherein the substrate
15 comprises a flexible plastic.
32. The process according to claim 31, wherein the flexible plastic comprises polyethylene terephthalate (PET).
33. The process according to any one of claims 22 to 32, wherein the resistivity of the copper film is 50 $\mu\Omega\cdot\text{cm}$ or less.

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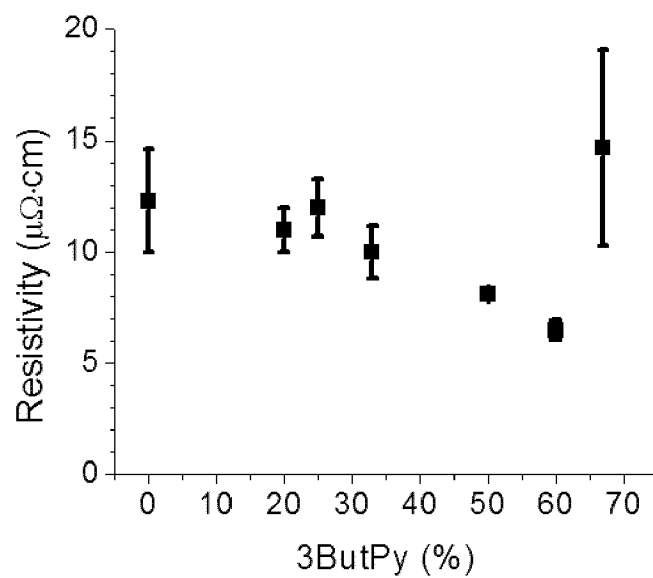


Fig. 1A

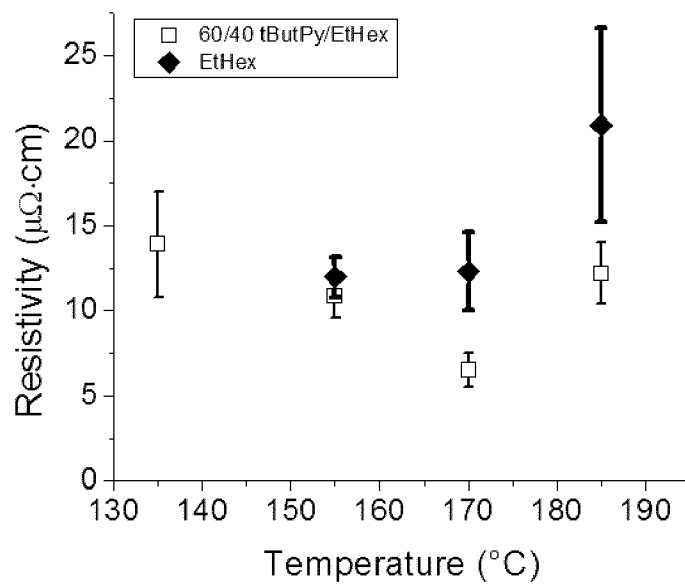


Fig. 1B

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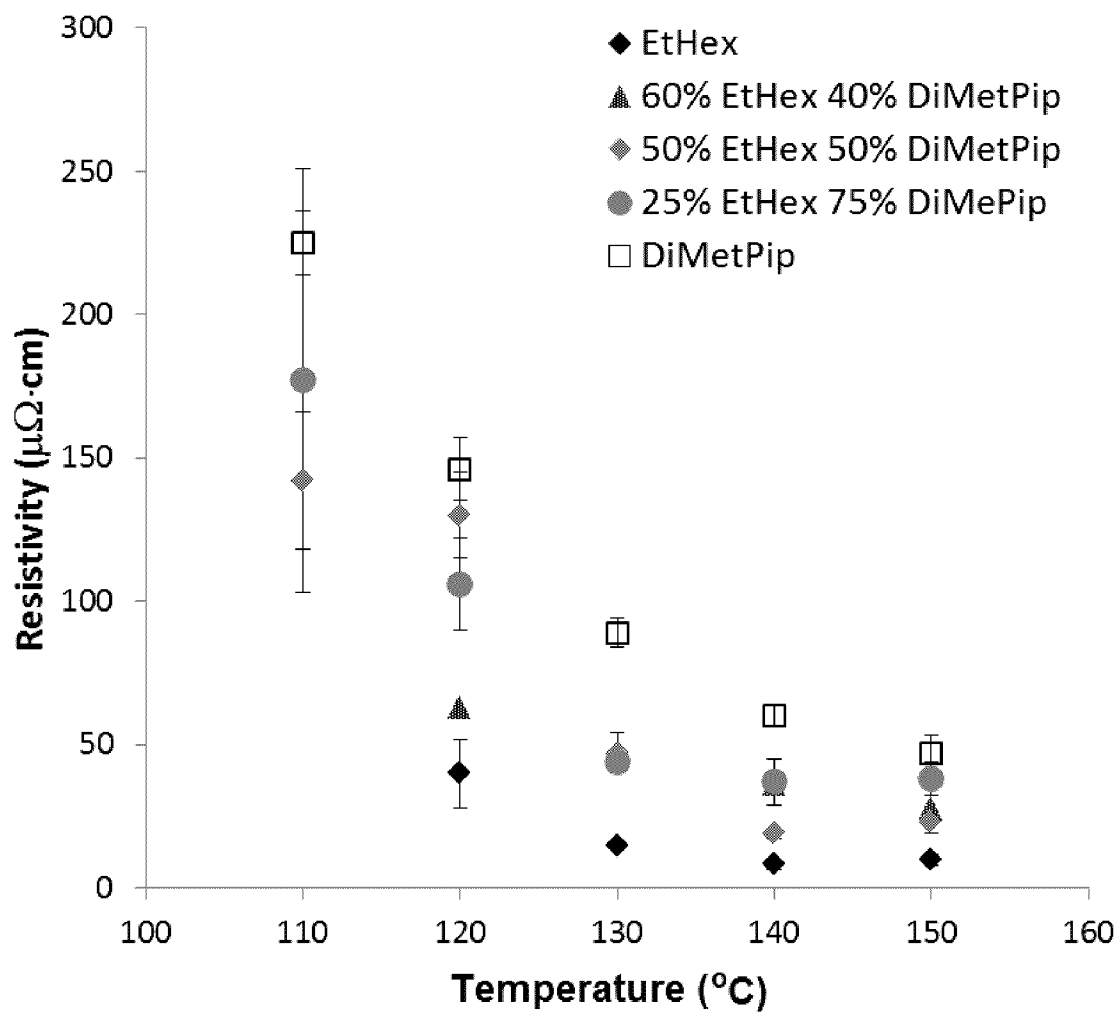


Fig. 2

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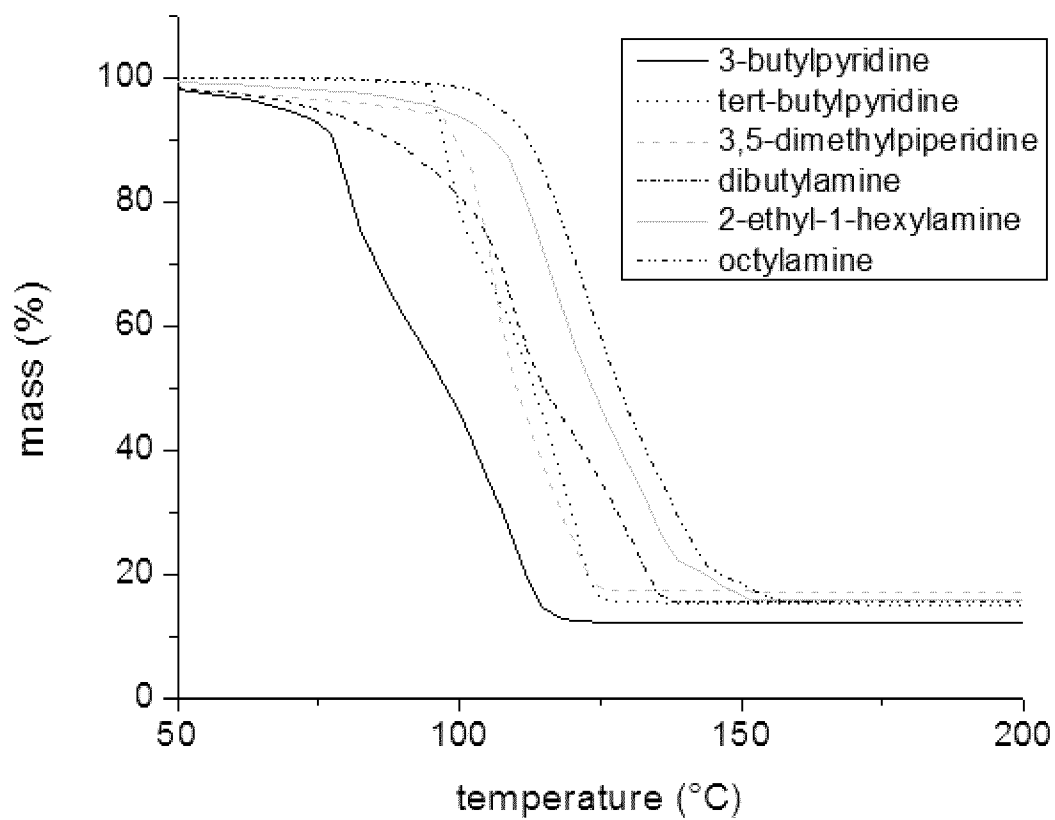


Fig. 3A

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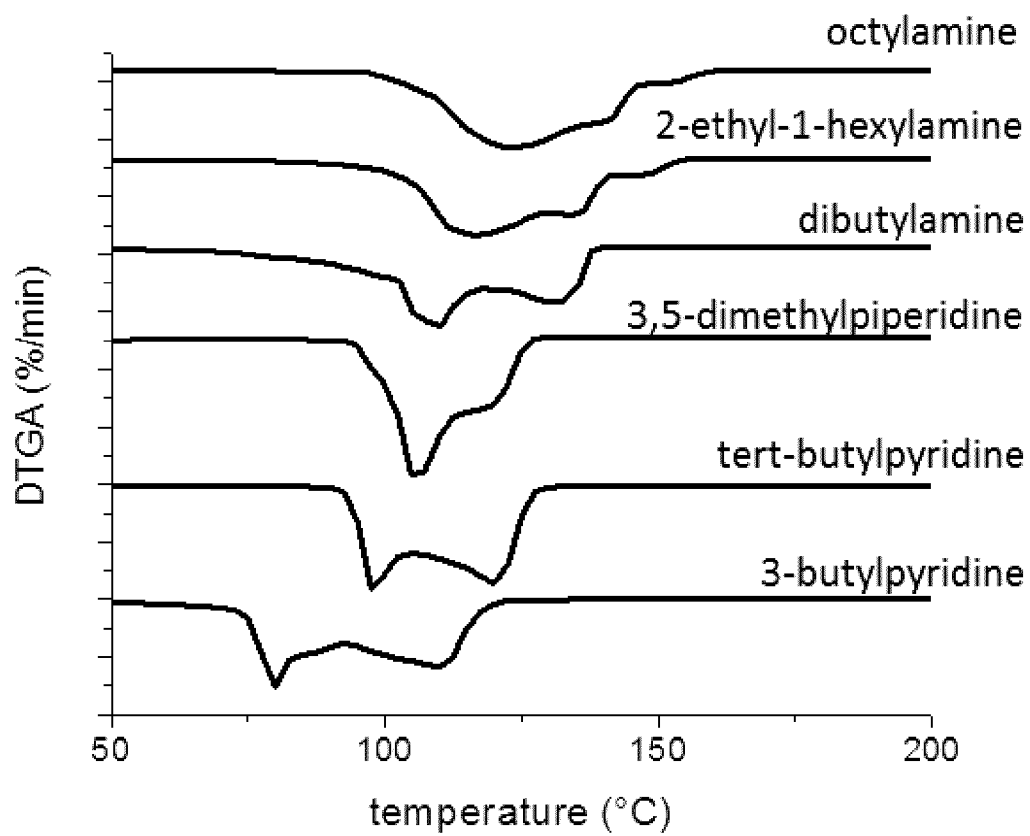


Fig. 3B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050091

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C07C 211/65** (2006.01), **C01G 3/00** (2006.01), **C07D 211/12** (2006.01), **C07D 213/16** (2006.01),
C09D 11/52 (2014.01), **H05K 1/03** (2006.01) (more IPCs on the last page)

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)

C07C 211 (2006.01), **C01G 3**(2006.01), **C07D 211**(2006.01), **C07D 213**(2006.01), **C09D 11**(2006.01), **H05K 1**(2006.01),
H05K 3 (2006.01)

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

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

STN (Registry file, CAPLUS), Questel Orbit, Scopus
 Keywords : copper, complexes, film, amine, imine, ink, formate, conductivity

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Yabuki A. et al. "Electrically conductive copper film prepared at low temperature by thermal decomposition of copper amine complexes with various amines" <i>Materials Research Bulletin</i> 47 (2012) 4107-4111. The whole document	1-13, 15-33
Y	WO 2014/010328 A1 (IIDA, Shusaku et al.) 16 January 2014 (16-01-2014) (of record, EP 2871260 A1 used as English equivalent) Claims 1, 2, 6, 8, 10-17; Reference Examples 1-7; Example 24; Tables 3, 4; paragraphs [0068], [0070]	1-13, 15-33
X	Kamysnyy A. et al. "Metal-based Inkjet Inks for Printed Electronics" <i>The Open Applied Physics Journal</i> 2011, 4 , 19-36. Page 26, right column, third paragraph; Fig. (8)	14

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

☒ See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	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 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 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
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Date of the actual completion of the international search
07 April 2016 (07-04-2016)

Date of mailing of the international search report
25 April 2016 (25-04-2016)

Name and mailing address of the ISA/CA
 Canadian Intellectual Property Office
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 Gatineau, Quebec K1A 0C9
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Authorized officer

May Ling Nung (819) 639-9347

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050091**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050091

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/095701 A1 (Bradley A Z. et al.) 20 November 2003 (20-11-2003) Examples 1, 5, 7, 8	14
X	CN 101519356 A (WU, Xinyan et al.) 02 September 2009 (02-09-2009) Claim 5; Example 7	14
X	Park, Kyung-Ho et al. "Remarkably Volatile Copper (II) Complexes of N,N'-Unsymmetrically Substituted ,1,3-Diketiminates as Precursors for Cu Metal Deposition via CVD or ALD" <i>Journal of American Chemical Society</i> 2005 , 127, 933-9331. The whole document	14
P,X	JP 2015-187259 (Anai, Kei et al.) 29 October 2015 (29-10-2015) Abstract; Example 11	14
P,Y	KR 2015/0085332 A (Lee B.Y. et al.) 23 July 2015 (23-07-2015)	1-13, 15-33
P,A	WO 2015/192248 (Kell, Arnold et al.) 23 December 2015 (23-12-2015) The whole document	1-33
A	TW 201437299 A (Kano, T. et al.) 01 October 2014 (01-10-2014) Paragraphs 0052-0069	1-33

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CA2016/050091

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2014010328A1	16 January 2014 (16-01-2014)	WO2014010328A1 EP2871260A1 CN104471108A IN149DEN2015A KR20150034168A TW201406991A US2015189748A1	16 January 2014 (16-01-2014) 13 May 2015 (13-05-2015) 25 March 2015 (25-03-2015) 12 June 2015 (12-06-2015) 02 April 2015 (02-04-2015) 16 February 2014 (16-02-2014) 02 July 2015 (02-07-2015)
WO03095701A1	20 November 2003 (20-11-2003)	WO03095701A1 WO03095701A8 AU2003210599A1 CN1617948A CN100360709C EP1466032A1 JP2005520053A KR20040077733A US2003232142A1 US6939578B2 US2005158479A1 US7087774B2 US2005107283A1 US7186835B2 US2006237718A1 US7268365B2 US2005267305A1 US7388113B2 US2005003075A1	20 November 2003 (20-11-2003) 21 May 2004 (21-05-2004) 11 November 2003 (11-11-2003) 18 May 2005 (18-05-2005) 09 January 2008 (09-01-2008) 13 October 2004 (13-10-2004) 07 July 2005 (07-07-2005) 06 September 2004 (06-09-2004) 18 December 2003 (18-12-2003) 06 September 2005 (06-09-2005) 21 July 2005 (21-07-2005) 08 August 2006 (08-08-2006) 19 May 2005 (19-05-2005) 06 March 2007 (06-03-2007) 26 October 2006 (26-10-2006) 11 September 2007 (11-09-2007) 01 December 2005 (01-12-2005) 17 June 2008 (17-06-2008) 06 January 2005 (06-01-2005)
CN101519356A	02 September 2009 (02-09-2009)	None	
JP2015187259A	29 October 2015 (29-10-2015)	None	
KR 20150085332 A	23 July 2015 (23-07-2015)	None	
WO2015192248A1	23 December 2015 (23-12-2015)	None	
TW201437299A	01 October 2014 (01-10-2014)	TW201437299A JP2014182913A WO2014148091A1	01 October 2014 (01-10-2014) 29 September 2014 (29-09-2014) 25 September 2014 (25-09-2014)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CA2016/050091

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

Invention I: Claims 1-13, and 15-33

A copper precursor composition, a copper ink comprising said composition and a substrate comprising said ink, and a process for producing a metallic copper film. Said composition comprising: a first copper complex comprising an imine or a first cyclic amine coordinated to a first copper precursor compound; and, a second copper complex comprising a primary amine or a second cyclic amine coordinated to a second copper precursor compound, the copper precursor composition thermally degradable at a temperature lower than a comparable composition comprising only the second copper complex under otherwise the same conditions to produce a metallic copper film having a resistivity of about $200 \mu \Omega \text{cm}$ or less.

Invention II: Claims 14

A copper complex comprising an imine coordinated to a copper precursor compound.

The common concept linking the present set of claims is a copper complex comprising an imine coordinated to a copper precursor compound. However the prior art revealed that the common concept is known see for example WO 03/095701 (D4) disclosing 1,3-diimine copper complexes and Kyung-Ho Park et al.(D6) disclosing copper(II) complexes of N,N'-unsymmetrically substituted 1,3-diketimines and their use in copper metal deposition.

Thus, the common concept is known and therefore not novel. It follows that the common concept can also not be inventive. Hence there is no single common inventive concept and therefore the requirements of unity are not met (Rule 13.1 PCT)

H05K 1/09 (2006.01), *H05K 3/12* (2006.01)