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(54) Title: PRESERVATIVE COMPOSITIONS FOR WOOD AND LIKE MATERIALS

(57) Abstract: Disclosed are compositions and processes for the preservation of porous materials, particularly porous fibrous material, such as wood, wood composites, other processed wood materials, paper, board, card, textiles, rope, cordage and leather Also for horticultural and agricultural application to plants or growing media prevent the growth and spread of fungal and other disease The compositions contain salts of one or more preservative metals and carboxylic acids having one or a plurality of hydroxyl groups rendered soluble by means of complex formation with boric acid or a water soluble salt thereof Application of the compositions of this invention to the porous organic material may be by any means used with conventional preservative solutions, for example soaking, spraying, brushing and vacuum or pressure application or other contact of the solution with the material to be treated.



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Title: PRESERVATIVE COMPOSITIONS FOR WOOD AND LIKE MATERIALS**FIELD**

5 The present technology relates to preservatives containing complexes of salts of preservative metals with organic hydroxy acids and soluble boron compounds. The complexes are soluble in water, in aqueous solutions of water soluble boron compounds which may be the same or different to those forming the complex and also soluble in certain organic solvents such as glycols, and in glycol solutions of
10 glycol soluble boron compounds which may be the same or different to those forming the complex. The boron compounds impart additional preservative properties.

The technology further relates to a process of utilizing such preservatives for the preservation of porous materials, particularly porous fibrous materials, such as wood,
15 wood composites, other processed wood materials, paper, board, card, textiles, rope, cordage and leather. These materials are prone to natural spoilage by attack by insects, fungi, moulds, bacteria and other micro-organisms.

The technology yet further relates to a process for protecting seeds and growing
20 plants from fungal, insect, mould and bacterial attack.

BACKGROUND

Compounds of cobalt, iron, manganese, nickel and, more particularly, copper and zinc (hereinafter collectively referred to as "preservative metals") are established
25 preservatives for organic materials to prevent spoilage, decay and attack by pests. Such compounds, particularly those of copper, also have applications as agricultural and horticultural pesticides.

In order to apply the preservative metal compound to the porous materials in a
30 manner suitable for it to act as a preservative, it is desirable for the compound to be soluble in a carrier liquid which is capable of penetrating into the porous material.

Boron compounds in the form of boron oxide, boric acid and borate salts have a more recent history as wood preservatives, insecticides, fungicides and molluscicides replacing more toxic and environmentally undesirable materials such as chromates, arsenates, phenolic and organo-halogen pesticides, particularly poly-halogenated aromatic and cyclic compounds.

Boric acid (orthoboric acid and metaboric acid), borate salts, exemplified by borax (sodium tetraborate) and DOT (disodium octaborate tetrahydrate), are nowadays very widely used as they are effective, have low toxicity to higher life forms, have a small environmental impact at the concentrations normally used and are of relatively low cost.

To facilitate preservative activity against a wide range of spoilage organisms, it is advantageous to use more than one preservative agent. Mixtures of borates with the more usual salts of a preservative metal such as the sulfate, nitrate, chloride or acetate results in the formation of the insoluble borate salt of the preservative metal. Whilst these borate salts may have some of the desired enhanced preservative properties they are of very low solubility and are thus difficult to apply into the body of the substrate and thus have a limited action. There is thus a need for a method of combining the active borate ion and preservative metals whilst maintaining solubility in water and/or commonly used solvents.

In order to formulate useful combinations of preservative metals compatible with borate compounds, prior art has been mainly concerned with the formation and use of ammine and amine complexes of the preservative metals. These complexes have a number of disadvantages including a foul, often overpowering odor and toxicity. This has been partially overcome by the use of alkanolamines but these can introduce other problems. The release of odorous, potentially toxic vapors of ammine and amine complexes gives rise to unpleasant working conditions for operatives and requires the provision of extraction equipment or an enclosed working space. The

release of ammonia and amines to the atmosphere on a large scale causes pollution and has an adverse effect on the environment.

There is thus a further need for water and glycol soluble preservative metal/borate combinations without the disadvantages described.

SUMMARY

We have discovered that the borate complexes of metal salts are highly soluble in water, aqueous solutions and glycol-based solvents thus providing a means of utilizing a preservative metal in the presence of the borate ion, facilitating the formation of concentrated solutions. Furthermore, we have unexpectedly discovered that compositions of the borate complexes of metal salts are stable in the presence of excess borate ions, thus the metal salt-borate complexes can be added to other borate containing preservatives which may be already in widespread use.

I am repeating the foregoing paragraph here to ensure that it is clear that the application is a selection patent application.

The compositions may be used for the preservation of porous organic materials, such as wood, wood composites and other processed wood materials, textiles, ropes, cordage, paper, card and leather. The compositions also have applications in agriculture and horticulture for protecting seeds and growing plants from fungal, insect, mould and bacterial attack and for application to compost and other growth medium to protect against fungal, insect, mould and bacterial attack.

The compositions can be applied to the substrate by conventional processes such as immersion, brushing, spraying, steeping, vacuum application, pressure application, combined vacuum and pressure application, steeping in combination with pressure change and the like.

The preservative compositions can be offered, for example, but not limited to:

(i) as liquid concentrate form for application as such, for dilution in water or other suitable solvent or incorporation into other preservative products.

(ii) in dilute ready to use form for application as such or incorporation into processed products.

(iii) as a pre-reacted complex in solid form for the preparation of a concentrated aqueous solution for addition to other preservative preparations, for further dilution with water for application as is, or as a dilute ready to use preservative solution.

(iv) as a pre-reacted complex in powder or granular form for addition to wood composites and similar materials during manufacture.

(v) as a physical mixture or separate components in solid form for the *in situ* preparation of a solution for addition to other preservative preparations, for further dilution with water for application as is, or as a dilute ready to use preservative solution.

In one embodiment, a composition for use as a preservative is provided, comprising:

(a) a metal salt, the metal salt selected from at least one of cobalt, iron, manganese, nickel, copper, zinc;

(b) at least one organic acid comprising at least two carbon atoms, at least one carboxylic acid functional group and at least one hydroxyl group functional group per molecule; and

(c) at least one water soluble boron-containing compound,

wherein the composition comprises complexes.

In one aspect, the metal salt is a salt of copper, zinc or copper and zinc.

In another aspect, the metal salt is zinc.

In another aspect, the metal salt is copper.

In another aspect, the organic acid is an aliphatic monocarboxylic acid, a dicarboxylic acid or a tricarboxylic acid comprising at least one hydroxyl functional group per molecule.

In another aspect, the organic acid comprises one hydroxyl functional group per molecule.

5 In another aspect, the organic acid is a monocarboxylic acid.

In another aspect, the organic acid is a dicarboxylic acid.

In another aspect, the organic acid is a tricarboxylic acid.

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In another aspect, the organic acid is selected at least one of:

(i) glycolic (hydroxyacetic) acid; lactic (2-hydroxypropionic) acid,

(ii) gluconic acid (pentahydroxyhexanoic acid); glucoheptonic acid (glucose monocarboxylic acid),

15 (iii) malic acid (hydroxybutanedioic acid),

(iv) tartaric acid (2,3-dihydroxybutanedioic acid), its isomers, half salts; glucaric acid (tetrahydroxy-hexane-1,6-dioic acid) acid, its isomers, half salts; galactaric acid, its isomers, half salts, and

(v) citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

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In another aspect, the organic acid is glycolic (hydroxyacetic) acid; lactic (2-hydroxypropionic) acid and mixtures thereof.

In another aspect, the organic acid is gluconic acid (pentahydroxyhexanoic acid);

25 glucoheptonic acid (glucose monocarboxylic acid) and mixtures thereof.

In another aspect, the organic acid is malic acid (hydroxybutanedioic acid).

In another aspect, the organic acid is tartaric acid (2,3-dihydroxybutanedioic acid), its

30 isomers, half salts; glucaric acid (tetrahydroxy-hexane-1,6-dioic acid) acid, its

isomers, half salts and mixtures thereof; galactaric acid, its isomers, half salts and mixtures thereof.

In another aspect, the organic acid is citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

In another aspect, the boron containing compounds are selected from at least one of boron oxide, boric acid, metaboric acid, orthoboric acid, borax decahydrate, borax pentahydrate, anhydrous borax, sodium borates, potassium borates, lithium borates, ammonium borates, amine borates, and alkanolamine borates.

In another aspect, the boron containing compounds are selected from at least one of disodium octaborate, sodium pentaborate, sodium metaborate, potassium pentaborate, ammonium diborate, and ammonium pentaborate.

In another aspect, the composition further comprises a solvent.

In another aspect, the solvent is an aqueous solvent or a glycol-based solvent.

In another aspect, the solvent is water.

In another aspect, the solvent is selected from at least one of ethylene glycol (ethane-1,2-diol), diethylene glycol (2,2'-oxybisethanol), triethylene glycol (2,2'-ethylenedioxybis[ethanol]), polyethylene glycols of molecular weights with the range 200 – 6000, propylene glycol (propane-1,2-diol), dipropylene glycol (oxybispropanol), water soluble polypropylene glycols, trimethylene glycol (propane-1,3-diol), glycerine (propane-1,2,3-triol), hexamethylene glycol (1,6-hexanediol), pentamethylene glycol (1,5-pentanediol), 1,3-butylene glycol (1,3-butanediol), and 2,3-butylene glycol (2,3-butanediol).

In another aspect, the composition further comprises a surfactant.

In another aspect, the surfactant is selected from ethylene glycol/propylene glycol copolymer surfactants, polyethylene glycol ester surfactants, polyethylene ether surfactants, other non-ionic surfactants, anionic surfactants, cationic surfactants, zwitterionic surfactants, silicone glycol surfactants, and fluorinated surfactants.

In another aspect, the composition is a solid.

In another aspect, the solid is granular or powdered.

In another aspect, the composition further comprises a second preservative.

In another aspect, the second preservative comprises borate ion.

In another embodiment, a method of preparing a composition for use as a preservative is provided comprising:

(i) selecting:

(a) a metal salt or a precursor for the production of a metal salt, the metal salt selected from at least one of cobalt, iron, manganese, nickel, copper, and zinc;

(b) an organic acid or a compound for the production of an organic acid, the organic acid having at least two carbons, at least one carboxylic acid functional group and at least one hydroxyl functional group;

(ii) preparing the metal salt; and

(iii) complexing the metal salt by the addition of a boron containing compound to prepare a complex.

In one aspect, the method comprises selecting an aliphatic monocarboxylic acid, a dicarboxylic acid or a tricarboxylic acid comprising at least one hydroxyl functional group per molecule or a compound for the production of an aliphatic monocarboxylic acid, a dicarboxylic acid or a tricarboxylic acid comprising at least one hydroxyl functional group per molecule.

In another aspect, the method comprises selecting at least one of:

- (i) glycolic (hydroxyacetic) acid; lactic (2-hydroxypropionic) acid,
- (ii) gluconic acid (pentahydroxyhexanoic acid); glucoheptonic acid (glucose monocarboxylic acid),
- (iii) malic acid (hydroxybutanedioic acid),
- (iv) tartaric acid (2,3-dihydroxybutanedioic acid), its isomers, half salts; glucaric acid (tetrahydroxy-hexane-1,6-dioic acid) acid, its isomers, half salts; galactaric acid, its isomers, half salts, and
- (v) citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

In another aspect, the method comprises complexing the metal salt with at least one of boron oxide, boric acid, metaboric acid, orthoboric acid, borax decahydrate, borax pentahydrate, anhydrous borax, sodium borates, potassium borates, lithium borates, ammonium borates, amine borates, or alkanolamine borates.

In another aspect, the method further comprises adding a solvent.

In another aspect of the method the solvent is water.

In another aspect of the method the solvent is selected from at least one of ethylene glycol (ethane-1,2-diol), diethylene glycol (2,2'-oxybisethanol), triethylene glycol (2,2'-ethylenedioxybis[ethanol]), polyethylene glycols of molecular weights with the range 200 – 6000, propylene glycol (propane-1,2-diol), dipropylene glycol (oxybispropanol), water soluble polypropylene glycols, trimethylene glycol (propane-1,3-diol), glycerine (propane-1,2,3-triol), hexamethylene glycol (1,6-hexanediol), pentamethylene glycol (1,5-pentanediol), 1,3-butylene glycol (1,3-butanediol), and 2,3-butylene glycol (2,3-butanediol).

In another aspect, the method further comprises adding a surfactant.

In another aspect, the method further comprises drying the complex to form a solid.

In another aspect, the method further comprises powdering or granulating the solid.

- 5 In another aspect, the method further comprises applying the composition to a substrate.

In another aspect of the method the composition is applied by brushing, spraying or steeping.

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In another aspect of the method the composition is applied by steeping.

In another aspect, the method further comprises increasing or decreasing pressure, or both increasing and decreasing pressure during steeping.

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In another aspect of the method the substrate is selected from seeds, plant material or growth medium.

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In another aspect of the method the substrate is selected from porous fibrous materials, selected from wood, processed wood materials, paper, cardboard, textiles, rope, cordage, or leather.

In another aspect, the method further comprises adding a second preservative.

- 25 In another aspect of the method the second preservative comprises borate ion.

DETAILED DESCRIPTION

- 30 Component (a) of the composition is a preservative metal, preferably copper, zinc, cobalt, iron, manganese or nickel, more preferably copper, zinc or cobalt and most preferably copper. In situations where the color of the preservative of the present

technology and, in turn, the color of the item treated with the preservative is of concern, zinc is the preferred preservative metal.

Component (b) of the preservatives is a carboxylic acid with one or more carboxyl groups per molecule and one or more hydroxyl groups per molecule. Representative and non-limiting examples of acids within the meaning of the present technology are:

(i) Aliphatic monocarboxylic acids with one hydroxyl group: glycolic acid (hydroxyacetic acid), lactic acid (2-hydroxypropionic acid).

(ii) Aliphatic monocarboxylic acids with a plurality of hydroxyl groups: gluconic acid (pentahydroxyhexanoic acid), glucoheptonic acid (glucomonocarboxylic acid).

(iii) Aliphatic dicarboxylic acids with one hydroxyl group per molecule: malic acid (hydroxybutanedioic acid).

(iv) Aliphatic dicarboxylic acids with two hydroxyl groups: tartaric acid (2,3-dihydroxybutanedioic acid) and its isomers.

(v) Aliphatic dicarboxylic acids with four hydroxyl groups: glucaric acid (tetrahydroxyhexanedioic acid).

(vi) Aliphatic tricarboxylic acids with one hydroxyl group: citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

Combinations of two or more organic acids and/or salts of such acids may be used in carrying out the present technology and it is acceptable to use any known commercially available product. Isomers of these acids or mixtures of isomers are also within the scope of the present technology.

The salts of the preservative metals defined in (a) above and organic acids as defined in (b) above (hereinafter collectively referred to as "preservative salts") may be articles of commerce. Alternatively, the preservative salts may be prepared extemporaneously by conventional chemical methods known by those skilled in the art.

Component (c) of the preservatives of the present technology is a water soluble boron compound in the form of boric oxide, boric acid, borate salts, boronic salts and boronic esters. It is known that boric acid and borate salts form complexes with organic compounds that contain a plurality of hydroxyl groups. We have discovered
5 that the borate complexes of the preservative salts are highly soluble in water thus providing a means of utilizing the preservative metal in the presence of the borate ion, facilitating the formation of concentrated solutions. Furthermore, we have unexpectedly discovered that solutions of the borate complexes of preservative salts are stable in the presence of excess borate ions, thus the preservative salt-borate
10 complexes can be added to other borate containing preservative solutions which may be already in widespread use.

The solvent carrier for the solutions of the preservatives of the present technology is, for reasons of economy and convenience, water. Some advantage may be gained by
15 the use of a glycol solvent either alone or in combination with an aqueous solvent. Glycol solvents of particular merit for this application include ethylene glycol (ethane-1,2-diol), diethylene glycol (2,2'-oxybisethanol), triethylene glycol (2,2'-ethylenedioxybis[ethanol]), polyethylene glycols of molecular weights with the range 200 – 6000, propylene glycol (propane-1,2-diol), dipropylene glycol (oxybispropanol),
20 water soluble polypropylene glycols, trimethylene glycol (propane-1,3-diol), glycerine (propane-1,2,3-triol), hexamethylene glycol (1,6-hexanediol), pentamethylene glycol (1,5-pentanediol), 1,3-butylene glycol (1,3-butanediol), 2,3-butylene glycol (2,3-butanediol), 2-ethoxyethanol, 2-(2-ethoxyethoxyethanol), butoxyethanol, 2-(2-butoxyethoxy)ethanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, methoxy-
25 propoxypropanol, ethoxypropoxypropanol and related solvents.

The penetration of the preservatives of the present technology into the deeper parts of the porous organic material, particularly porous fibrous material, such as wood, wood composites and other processed wood materials, textiles, ropes, cordage and
30 leather may be enhanced by the inclusion of a detergent or surfactant into the preservatives of the present technology. Non-limiting examples of surfactants suitable

for this application include ethylene glycol/propylene glycol copolymer surfactants, polyethylene glycol ester surfactants, polyethylene ether surfactants, other non-ionic surfactants, anionic surfactants, cationic surfactants, zwitterionic surfactants, silicone glycol surfactants, fluorinated surfactants.

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The present technology thus further consists of a process for the treatment of a porous organic material, particularly porous fibrous material, such as wood, wood composites and other processed wood materials, textiles, ropes, cordage and leather by applying to the material an aqueous, a glycol or aqueous/glycol solution of the technology or a composition containing said solution.

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The present technology still further consists of a process for the treatment during the processing of porous organic materials, particularly wood composites and other processed wood materials, by incorporating the preservatives of the present technology, preferably in powder or granular form, into the porous organic materials during manufacture.

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Application of the preservatives of the present technology to the porous organic material may be by any means used with conventional preservative solutions, for example soaking, spraying, brushing, and vacuum or pressure application or other contact of the solution with the material to be treated. Treatment of wood is preferably by a pressure method and commercial units and systems are available. Application of the solution by simple soaking or steeping requires sufficient time for the solution to penetrate and, in the case of timber of large bulk, this can be prolonged. Unseasoned timber may be treated by diffusion or by any other well known process that allows diffusion into wet wood.

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Although the solutions of the preservatives of the present technology are of particular value in the treatment of solid timber and, for this reason, the treatment of solid timber has been described in detail above, they may also, by adoption of suitable application techniques, be used for the treatment of wood chips, fiber board, particle board,

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plywood or other fibrous materials, including paper pulp, paper, board, card, textiles, rope cordage and leather and means for treating these materials are well known to those skilled in the art.

- 5 The aqueous solutions of the preservatives of the present technology, particularly those containing copper as the preservative metal, are also valuable for the treatment of seeds or growing plants in agriculture, horticulture or home garden use to prevent the growth and spread of fungal and other plant or growth medium disease. The solutions may be applied by any method used for the application of known fungicidal
10 solutions, but are most preferably applied by spraying. Application of the preservatives of the present technology in solid form as powder or granules to compost and other growth medium may also be made.

The technology is further illustrated by the following non-limiting Examples:

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EXAMPLE 1

- About 500g of copper sulfate pentahydrate was dissolved in a suitable quantity of hot water. A stoichiometric quantity of a solution of potassium sodium tartrate was then mixed into the hot copper sulfate solution with stirring. Copper tartrate precipitated
20 from the mixture as a pale blue powder. After cooling, the precipitate was washed several times with water to remove sulfate ions and vacuum filtered to leave a paste containing 60 – 70% copper tartrate trihydrate.

The solids content of the paste was determined by drying a sample to constant weight at 110°C.

- 25 A quantity of the paste equivalent to 420g copper tartrate trihydrate (=100g copper) was mixed with 200g borax (sodium tetraborate decahydrate) and sufficient water to make 1,000g. The mixture was stirred and heated to facilitate the formation of the borate/tartrate complex. The resulting product contained about 10% of copper and was a clear, deep blue, viscous solution miscible with water and solutions of borate
30 salts.

EXAMPLE 2

About 500g zinc sulfate heptahydrate was dissolved in a suitable quantity of hot water. A stoichiometric quantity of a solution of potassium sodium tartrate was then mixed into the hot zinc sulfate solution with stirring. Zinc tartrate precipitated from the mixture as a white powder. After cooling, the precipitate was washed several times with water to remove sulfate ions and vacuum filtered to leave a paste containing 60 – 70% zinc tartrate dihydrate.

The solids content of the paste was determined by drying a sample to constant weight at 110°C.

A quantity of the paste equivalent to 420g zinc tartrate dihydrate (=100g zinc) was mixed with 200g borax (sodium tetraborate decahydrate) and sufficient water to make 1,000g. The mixture was stirred and heated to facilitate the formation of the borate/tartrate complex. The resulting product contained about 10% of zinc was a clear, colorless, viscous solution miscible with water and solutions of borate salts.

EXAMPLE 3

500g copper gluconate was mixed with 200g borax decahydrate and 300g water. The mixture was stirred and heated to about 60°C to dissolve the solids and facilitate the reaction to form the borate/gluconate complex. The resulting product contained about 7% copper and was a clear, bluish-green, viscous liquid miscible with water and solutions of borate salts.

EXAMPLE 4

500g zinc gluconate was mixed with 200g borax decahydrate and 300g water. The mixture was stirred and heated to about 60°C to form the borate/gluconate complex. The resulting product contained about 7% zinc and was a clear, colorless, viscous liquid miscible with water and solutions of borate salts.

EXAMPLE 5

360g copper tartrate tetrahydrate in powder form was suspended in 440g water and 200g borax decahydrate added. The mixture was stirred and heated to about 80°C

and allowed to react to form the borate/tartrate complex. Water lost by evaporation was replaced. The resulting product contained about 8% copper and was a clear, deep blue, viscous solution miscible with water and solutions of borate salts.

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EXAMPLE 6

500g copper gluconate was mixed with 250g borax decahydrate and 100g water. The mixture was stirred and heated to about 60°C to form the gluconate/borate complex. The solids dissolved to form a clear, very dark green, viscous mass. The reaction product was spread on to a flexible polyethylene sheet and the excess moisture was allowed to evaporate. The resultant product was a dark green, brittle, glass-like solid easily crushed to form granules or powder. The product was very soluble in water and solutions of borate salts, forming a blue-green, clear to slightly hazy solution. The solid contained about 9% copper.

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EXAMPLE 7

500g zinc gluconate was mixed with 250g borax decahydrate and 100g water. The mixture was stirred and heated to about 60°C to form the gluconate/borate complex. The solids dissolved to form a clear, colorless, viscous mass. The reaction product was spread on to a flexible polyethylene sheet and the excess moisture was allowed to evaporate. The resultant product was a colorless, brittle, glass-like solid easily crushed to form granules or powder. The product was very soluble in water and solutions of borate salts, forming a colorless, clear to slightly hazy solution. The solid contained about 9% zinc.

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EXAMPLE 8

About 100g copper carbonate of commerce (equivalent to 50g Cu) was slowly added to about 625g of warm gluconic acid (50% solution of commerce). When the evolution of carbon dioxide had ceased and the copper carbonate dissolved, 200g borax decahydrate was added and the solution made up to 1,000g with water. The resulting product contained about 5% copper and was a clear to slightly hazy, bluish-green, viscous liquid miscible with water and solutions of borate salts.

In addition, various known additives may be combined with the preservatives formulated according to the present technology without substantially affecting the preservative capability of the present technology. For example, other preservative compounds and compositions may be added to the preservatives of the present technology. Coloring agents, waxes, resins, aqueous solutions, various emulsions and suspensions and other ingredients may be added to the preservatives of the present technology where such additional properties are desirable.

- 10 The preservatives of the present technology may also be used to treat growth medium such as compost, living plants and seeds to prevent and/or treat fungal, insect, mould and bacterial attack. For this purpose the treatment solution would preferably be applied by spraying methods but the solutions may be applied by any method commonly used to apply known pesticides to growth medium, seed and plants, agricultural and horticultural crops. For the treatment of growth medium, the preservatives of the present technology in solid form, as demonstrated in Examples 6 and 7 may be preferred.

- 20 From the foregoing, it will be appreciated that, although specific embodiments of the present technology have been described herein for the purposes of illustration, various modifications may be made without deviating from the spirit and scope of the technology. Accordingly, the present technology is not limited except as by the appended Claims.

CLAIMS

- 5 1. A composition for use as a preservative, the composition comprising:
- (a) a metal salt, the metal salt selected from at least one of cobalt, iron, manganese, nickel, copper, zinc;
 - (b) at least one organic acid comprising at least two carbon atoms, at least one carboxylic acid functional group and at least one hydroxyl group functional
 - 10 group per molecule; and
 - (c) at least one water soluble boron-containing compound,
- wherein the composition comprises complexes.
2. The composition of claim 1 wherein the metal salt is a salt of copper, zinc or
- 15 copper and zinc.
3. The composition of claim 2 wherein the metal salt is zinc.
4. The composition of claim 2 wherein the metal salt is copper.
- 20 5. The composition of any one of claims 1 to 4, wherein the organic acid is an aliphatic monocarboxylic acid, a dicarboxylic acid or a tricarboxylic acid comprising at least one hydroxyl functional group per molecule.
- 25 6. The composition of claim 5, wherein the organic acid comprises one hydroxyl functional group per molecule.
7. The composition of claim 5 or 6, wherein the organic acid is a monocarboxylic acid.
- 30 8. The composition of claim 5 or 6, wherein the organic acid is a dicarboxylic acid.

9. The composition of claim 5 or 6, wherein the organic acid is a tricarboxylic acid.

10. The composition of claim 5, wherein the organic acid is selected at least one of:

(i) glycolic (hydroxyacetic) acid; lactic (2-hydroxypropionic) acid,

5 (ii) gluconic acid (pentahydroxyhexanoic acid); glucoheptonic acid (glucose monocarboxylic acid),

(iii) malic acid (hydroxybutanedioic acid),

(iv) tartaric acid (2,3-dihydroxybutanedioic acid), its isomers, half salts; glucaric acid (tetrahydroxy-hexane-1,6-dioic acid) acid, its isomers, half salts; galactaric acid, its isomers, half salts, and

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(v) citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

11. The composition of claim 10 wherein the organic acid is glycolic (hydroxyacetic) acid; lactic (2-hydroxypropionic) acid and mixtures thereof.

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12. The composition of claim 10 wherein the organic acid is gluconic acid (pentahydroxyhexanoic acid); glucoheptonic acid (glucose monocarboxylic acid) and mixtures thereof.

13. The composition of claim 10 wherein the organic acid is malic acid (hydroxybutanedioic acid).

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14. The composition of claim 10 wherein the organic acid is tartaric acid (2,3-dihydroxybutanedioic acid), its isomers, half salts; glucaric acid (tetrahydroxy-hexane-1,6-dioic acid) acid, its isomers, half salts and mixtures thereof; galactaric acid, its isomers, half salts and mixtures thereof.

25

15. The composition of claim 10 wherein the organic acid is citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

30

16. The composition of any one of claims 1-15 wherein the boron containing compounds are selected from at least one of boron oxide, boric acid, metaboric acid,

orthoboric acid, borax decahydrate, borax pentahydrate, anhydrous borax, sodium borates, potassium borates, lithium borates, ammonium borates, amine borates, and alkanolamine borates.

5 17. The composition of claim 16 wherein the boron containing compounds are selected from at least one of disodium octaborate, sodium pentaborate, sodium metaborate, potassium pentaborate, ammonium diborate, and ammonium pentaborate.

10 18. The composition of any one of claims 1 to 17, further comprising a solvent.

19. The composition of claim 18 wherein the solvent is an aqueous solvent or a glycol-based solvent.

15 20. The composition of claim 19 wherein the solvent is water.

21. The composition of claim 19 wherein the solvent is selected from at least one of ethylene glycol (ethane-1,2-diol), diethylene glycol (2,2'-oxybisethanol), triethylene glycol (2,2'-ethylenedioxybis[ethanol]), polyethylene glycols of molecular weights with
20 the range 200 – 6000, propylene glycol (propane-1,2-diol), dipropylene glycol (oxybispropanol), water soluble polypropylene glycols, trimethylene glycol (propane-1,3-diol), glycerine (propane-1,2,3-triol), hexamethylene glycol (1,6-hexanediol), pentamethylene glycol (1,5-pentanediol), 1,3-butylene glycol (1,3-butanediol), and 2,3-butylene glycol (2,3-butanediol).

25

22. The composition of any one of claims 1 to 21, further comprising a surfactant.

23. The composition of claim 22 wherein the surfactant is selected from ethylene glycol/propylene glycol copolymer surfactants, polyethylene glycol ester surfactants,
30 polyethylene ether surfactants, other non-ionic surfactants, anionic surfactants,

cationic surfactants, zwitterionic surfactants, silicone glycol surfactants, and fluorinated surfactants.

24. The composition of any one of claims 1 to 17 wherein the composition is a solid.

25. The composition of claim 24 wherein the solid is granular or powdered.

26. The composition of any one of claims 1 to 25 further comprising a second preservative.

27. The composition of claim 26 wherein the second preservative comprises borate ion.

28. A method of preparing a composition for use as a preservative, the method comprising:

(i) selecting:

(a) a metal salt or a precursor for the production of a metal salt, the metal salt selected from at least one of cobalt, iron, manganese, nickel, copper, and zinc;

(b) an organic acid or a compound for the production of an organic acid, the organic acid having at least two carbons, at least one carboxylic acid functional group and at least one hydroxyl functional group;

(ii) preparing the metal salt; and

(iii) complexing the metal salt by the addition of a boron containing compound to prepare a complex.

29. The method of claim 28 comprising selecting an aliphatic monocarboxylic acid, a dicarboxylic acid or a tricarboxylic acid comprising at least one hydroxyl functional group per molecule or a compound for the production of an aliphatic monocarboxylic acid, a dicarboxylic acid or a tricarboxylic acid comprising at least one hydroxyl functional group per molecule.

30. The method of claim 29 comprising selecting at least one of:

- (i) glycolic (hydroxyacetic) acid; lactic (2-hydroxypropionic) acid,
- (ii) gluconic acid (pentahydroxyhexanoic acid); glucoheptonic acid (glucose monocarboxylic acid),
- 5 (iii) malic acid (hydroxybutanedioic acid),
- (iv) tartaric acid (2,3-dihydroxybutanedioic acid), its isomers, half salts; glucaric acid (tetrahydroxy-hexane-1,6-dioic acid) acid, its isomers, half salts; galactaric acid, its isomers, half salts, and
- (v) citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid).

10 31. The method of any one of claims 28 to 30 comprising complexing the metal salt with at least one of boron oxide, boric acid, metaboric acid, orthoboric acid, borax decahydrate, borax pentahydrate, anhydrous borax, sodium borates, potassium borates, lithium borates, ammonium borates, amine borates, or alkanolamine borates.

15 32. The method of any one of claims 28 to 31, further comprising adding a solvent.

33. The method of claim 32 wherein the solvent is water.

20 34. The method of claim 32 wherein the solvent is selected from at least one of ethylene glycol (ethane-1,2-diol), diethylene glycol (2,2'-oxybisethanol), triethylene glycol (2,2'-ethyenedioxybis[ethanol]), polyethylene glycols of molecular weights with the range 200 – 6000, propylene glycol (propane-1,2-diol), dipropylene glycol (oxybispropanol), water soluble polypropylene glycols, trimethylene glycol (propane-
25 1,3-diol), glycerine (propane-1,2,3-triol), hexamethylene glycol (1,6-hexanediol), pentamethylene glycol (1,5-pentanediol), 1,3-butylene glycol (1,3-butanediol), and 2,3-butylene glycol (2,3-butanediol).

35. The method of any one of claims 28 to 34 further comprising adding a surfactant.

36. The method of any one of claims 28 to 31, further comprising drying the complex to form a solid.

37. The method of claim 34 further comprising powdering or granulating the solid.

5

38. The method of any one of claims 28 to 35, further comprising applying the composition to a substrate.

39. The method of claim 38 wherein the composition is applied by brushing, spraying
10 or steeping.

40. The method of claim 39 wherein the composition is applied by steeping.

41. The method of claim 40 further comprising increasing or decreasing pressure, or
15 both increasing and decreasing pressure during steeping.

42. The method of claim 38 wherein the substrate is selected from seeds, plant material or growth medium.

20 43. The method of claim 38 wherein the substrate is selected from porous fibrous materials, selected from wood, processed wood materials, paper, cardboard, textiles, rope, cordage, or leather.

44. The method of any one of claims 28 to 43, further comprising adding a second
25 preservative.

45. The method of claim 44 wherein the second preservative comprises borate ion.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2008/000076

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **B27K 3/52** (2006.01)

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)

B27K 3/52 , B27K 3/00 , B27K 3/02 , B27K 3/16 , B27K 3/22 , B27K 3/32 , B27K 3/36 , B27K 3/50 , B27K 3/52 , A01N 37/00
A01N 37/02 , A01N 55/00 , A01N 55/02 , A01N 55/08 , A01N 59/06 , A01N 59/14 , A01N 59/20 , C09K 15/02 , C09K 21/00

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)

QUESTEL-ORBIT , DELPHION (incl. Derwent) , CPD , WEST , SCOPUS , KNOVEL , STN (Caplus, Russiapat, Koreapat) , INTERNET

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	PL 147633 (NIESLOCHOWSKI, A et al.) 31 July 1989 (31-07-1989) abstract	1-4,16,28,31,38-43 18-27,32-45
X Y	CA 2114644 (RYAN, N et al.) 18 February 1993 (18-02-1993) page 6, first paragraph, lines 23-26; page 8, lines 25-27	1-16,26-33,43-45 1-16,18-33,32-45
X Y	WO 2006/039753 (CLARKE, C) 20 April 2006 (20-04-2006) page 5, lines 6-11; page 7, bottom paragraph; page 10, lines 22-25	1-17,26-33 1-16,28-45
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Y	US 4439572 (KINDRICK, R) 27 March 1984 (27-03-1984) the whole document	1-3,28

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

[X] See patent family annex.

* Special categories of cited documents :	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"B" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 April 2008 (21-04-2008)

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/CA2008/000076

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5338791 (Chaplin, D) 16 August 1994 (16-08-1994) the whole document	1-3,28

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Information on patent family members

International application No.
PCT/CA2008/000076

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