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(54) Title: FUNGICIDAL COMPOSITIONS AND METHODS FOR CONTROLLING PLANT PATHOGENS

(57) Abstract: The invention provides a synergistic composition, and a method for using it, for protecting agriculturally important species against a broad range of pathologies, particularly for treating of phytopathogenic diseases.

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FUNGICIDAL COMPOSITIONS AND METHODS FOR
CONTROLLING PLANT PATHOGENS

FIELD OF THE INVENTION

5 The present invention relates to novel fungicidal compositions for the treatment of phytopathogenic diseases, especially phytopathogenic fungi, and to a method for controlling phytopathogenic diseases.

10 **BACKGROUND OF THE INVENTION**

There are several major concerns these days when considering the treatment of plants against phytopathogenic organisms, e.g. phytopathogenic fungi. Said concerns include crop tolerance and fungi resistance. Over time
15 excessive dosing with fungicides in the treatment of plants has in certain cases triggered resistance to the fungicides by the treated fungi. In such cases when the dose is increased in order to control the fungi, there arises a concern for the tolerance of the plant. Thus, at certain
20 doses of fungicides the fungicide may in itself become phytotoxic to the plant. Furthermore, as doses increase, the adverse environmental impact of the fungicides increases. Hence, contamination of ground water and buildup of chemicals in the soil and plant may occur.

25 U.S. patent 6,689,392 to Agricare Ltd. discloses a novel composition for controlling growth of pathological organisms on plant wherein said composition contains (a) zinc and copper metal ions; (b) one or more chelating agent
30 selected from the group consisting of citric acid, citrates, and mixtures thereof; and (c) phosphorous acid, and/or salt or hydrate thereof. Said composition is

environmentally compatible in comparison to other chemical fungicides, in that the adverse environmental impact of said composition is significantly lower than said chemical fungicides. Commercial products marketed under the tradename "Calirus" are based on the disclosure of the '392 patent and is currently marketed in several countries. However, the activity of Calirus is relatively specific.

Accordingly, there is a long felt need for compositions and methods for treating phytopathogenic organisms in plants which do not induce resistance of the organism and do not affect plant tolerance, while also displaying environmental compatibility.

It is therefore an objective of the present invention to provide a compositions and methods for treating plant pathogens in a manner which reduces environmental impact, plant pathogen resistance while maintaining effective control of said pathogens without harming the plant.

It is yet a further objective of the present invention overcomes the disadvantages of the prior art.

Other objectives of the invention shall become apparent as the description proceeds.

SUMMARY OF THE INVENTION

The present invention provides a method for controlling plant pathogens, said method comprising applying to a plant, locus or plant propagation material thereof a combination of fungicides A) and B) wherein fungicide A) is an AG fungicidal composition as herein defined and B) is at

least one fungicide selected from a group of fungicides with protective and/or curative activity.

5 According to yet a further aspect of the present invention there is provided a synergistic fungicidal composition comprising a combination of fungicides A) and B) wherein fungicide A) is an AG fungicidal composition and B) is at least one fungicide selected from a group of fungicides with protective and/or curative activity. Optionally, the
10 compositions of the present invention further comprise a third pesticidal component C) wherein said pesticide C) is an insecticide or mixture thereof.

15 Further provided by the present invention is a tank mix containing a combination of fungicides A) and B) wherein fungicide A) is an AG fungicidal composition and B) is at least one fungicide selected from a group of fungicides with protective and/or curative activity. Optionally, said tank mix further comprises a third pesticidal component C)
20 wherein said pesticide C) is an insecticide or mixture thereof.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

25 The following description is illustrative of embodiments of the invention. The following description is not to be construed as limiting, it being understood that the skilled person may carry out many variations to the invention.

30 Surprisingly, the fungicidal activity obtained by the method, fungicidal compositions and tank mix according to the present invention are significantly higher than the sum of the activity of the individual fungicides. Thus, an

unforeseeable synergistic effect is present, and not merely an additive effect. Synergy may result in reduced application rates and/or an expansion of the activity spectrum of treated phytopathogens and/or an increase in the activity of the substances and compositions which can be used according to the invention; better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, better quality and/or a higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products are possible which exceed the effects which were actually to be expected.

Throughout the description the terms "fungicide" and "fungicidal composition" encompasses any plant-pathogen-controlling composition, algicide, antimicrobial agent, biopesticide, biocide, disinfectant and fumigant. Fungicidal activity relates to activities which prevent, control or cure fungi infestation. In this respect fungi infestation relates to infestation by organisms with pathological effects on the plant, plant propagation material or plant environment. The fungicidal compositions of the present invention may also be in the form of a formulation. The term controlling with respect to fungicidal activity as used herein refers to preventing and/or treating phytopathogenic fungal diseases.

Throughout the description percentage indicates weight by volume percentage where the formulations and/or tank mix

are liquid and weight by weight wherein the formulation is solid unless otherwise specifically indicated.

5 The present invention provides a method, composition and tank mix for controlling plant pathogens. Said invention is based on the surprising synergistic effect of fungicide A) and fungicide B) wherein fungicide A) is an AG fungicidal composition as herein defined and B) is at least one fungicide selected from a group of fungicides with
10 protective and/or curative activity. Optionally, said method, composition and tank mix further comprise a third component C) which is at least one pesticide, specifically an insecticide.

15 For the purpose of the methods, compositions and tank mixes of the present invention, fungicide A) is the fungicidal composition described and claimed in U.S. Pat. No. 6,689,392 incorporated herein by reference. Said composition claimed in the '392 patent as comprising (a)
20 zinc and copper metal ions; (b) one or more chelating agent selected from the group consisting of citric acid, citrates, and mixtures thereof; and (c) phosphorous acid, and/or salt or hydrate thereof. Specific AG compositions are commercially available under the tradenames "Calirus
25 150" which is a liquid formulation containing 150g/liter and "Calirus 980" which is a SP (soluble powder) formulation of 980g/kg.

30 Fungicide B) employed for the methods, compositions and tank mixes of the present invention is at least one fungicide selected from a group comprising of fungicides of protective and/or curative activity. Non-limiting examples

of B) fungicides are strobilurin fungicide, such as azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, trifloxystrobin, cyzofamid; an azole
5 fungicide, such as azaconazole, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil,
10 oxpoconazole, pefurazoate, penconazole, prochloraz, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole, diclobutrazol, etaconazole, furconazole, furconazole-cis and quinconazole; a phenyl pyrrole
15 fungicide, such as fenpiclonil and fludioxonil; an anilino-pyrimidine fungicide, such as cyprodinil, mepanipyrin and pyrimethanil; a morpholine fungicide, such as aldimorph, dimethimorph, dodemorph, fenpropimorph, tridemorph, fenpropidin, spiroxamine; piperalin, chlorothalonil;
20 famoxadone; fenamidone; benalaxyl; benalaxyl-M; benomyl; bitertanol; boscalid; carboxin; carpropamid; copper (diverse salts); copper ammoniumcarbonate; copper octanoate; copper oleate; copper sulphate; copper hydroxide; captan, cyazofamid; cymoxanil; diethofencarb;
25 dithianon; fenhexamide; fenoxycarb; fluazinam; flutolanil; folpet; fosetyl-Al, guazatine; hymexazole; iprodione; mancozeb; metalaxyl; mefenoxam; metrafenone; nuarimol; paclobutrazol; pencycuron; penthiopyrad; procymidone; pyroquilon; quinoxifen; silthiofam; sulfur; thiabendazole;
30 thiram; triazoxide; tricyclazole; proquinazid; captan; trinexapac-Ethyl; chlormequat chloride; ethephon; and acibenzolar-5-methyl; mineral oils and formulations thereof

with pesticidal activity, e.g. Enspray™ 99 by SK; and essential oils and formulations thereof, e.g. tea tree oil, Timorex™, and Timorex™ Gold.

5 Pesticide C) employed for the methods, tank mixes and compositions of the present invention is at least one insecticide. Non-limiting examples of suitable insecticide are selected from carbamate, macrocyclic lactone, neonicotinoid and pyrethroid insecticides. Non-limiting
10 examples of C) insecticides include: carbofuran, carbosulfan, abamectin, emamectin, spinosad, imadacloprid, dinotefuran, thiamethoxam, acetamiprid, thiacloprid, chloropyrifos, fipronil, indoxacarb, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, zeta-
15 cypermethrin, deltamethrin, tau-fluvalinate, and mixtures thereof.

The method of the present invention is based on the surprising synergistic activity exhibited by the
20 combination of fungicides A) and B). Said fungicides are commercially available in various formulations and sold under different tradenames. Thus, said fungicides have regulatory approval for use in accordance to the recommendations on the product label. The product label
25 specifies, inter alia the mode of application e.g. foliar spraying, the dosage/rate of application, the plants, crops and plant propagation material suitable for treatment and phytopathogens against which said fungicide is effective. According to the method of the present invention fungicides
30 A) and B) are applied at a total dose/rate which is 80% or less than the dose/rate recommended on the product label of the individual products. Thus, providing phytopathogenic

control equivalent or better than that provided by the application of only one of said A) or B) fungicides according to the label instructions.

5 According to a further aspect the present invention provides a method for controlling plant pathogens and pests in plant propagation materials, said method comprising applying to plant propagation material or locus of planting or sowing a combination of fungicides A) and B) and a
10 pesticide C) wherein fungicide A) is an AG fungicidal composition and B) is at least one fungicide selected from a group of fungicides with protective and/or curative activity and pesticide C) wherein pesticide C) is at least one pesticide selected from a group of insecticides.

15 According to a specific embodiment of the invention the fungicidal combinations of the present invention are applied in accordance with the presently described method at rates which can be varied within a relatively wide
20 range, depending on the kind of application. In the treatment of parts of plants, the application rates of the fungicidal combinations are generally between 0.1 and 10,000 g/ha, preferably between 10 and 1,000 g/ha. In the treatment of seeds, the application rates of active
25 compound combination are generally between 0.001 and 50 g per kilogram of seed, preferably between 0.01 and 10 g per kilogram of seed. In the treatment of the soil, the application rates of active compound combination are generally between 0.1 and 10 000 g/ha, preferably between 1
30 and 5 000 g/ha.

According to a particular embodiment of the method of the present invention the application of the fungicides may be carried out by separate, sequential or simultaneous application. Simultaneous application may be carried out by
5 applying separate preparations of fungicides A) and B) at the same time or by pre-mixing fungicides A) and B) together and then applying. Simultaneous application may further be carried out by applying a fungicidal composition comprising a combination of fungicides A) and B).

10

According to yet a further aspect of the present invention there is provided a synergistic fungicidal composition comprising a combination of fungicides A) and B) wherein fungicide A) is an AG fungicidal composition and B) is at
15 least one fungicide selected from a group of fungicides with protective and/or curative activity.

15

According to a further aspect the present invention provides a composition for controlling plant pathogens and
20 pests in plant propagation materials, said composition comprising fungicides A) and B) and a pesticide C) wherein fungicide A) is an AG fungicidal composition and B) is at least one fungicide selected from a group of fungicides with protective and/or curative activity and pesticide C)
25 is at least on insecticide.

20

25

The compositions according the present invention may be formulated in any suitable formulation depending on the crop and manner of application. Said compositions can be
30 formulated, for example, in the form of ready-to-spray solutions, powders and suspensions or in the form of highly concentrated aqueous, oily or other suspensions,

30

dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, and applied by spraying, atomizing, dusting, broadcasting or watering. Non-limiting examples of suitable formulations are: EC (Emulsifiable Concentrate), WP (Wettable Powder), SL (Soluble Liquid concentrate), SP (Soluble Powder), SC (Suspension Concentrate), CS (Capsule Suspensions) and WG (Water Dispersible granules). The selection of a particular formulation is within the expertise of the skilled artisan and falls within the scope of the preset invention. The use form depends on the intended purpose; in any case, it should ensure as fine and uniform a distribution as possible of the mixture according to the invention.

The formulations are prepared in a manner known per se, for example by adding solvents and/or carriers. It is usual to admix inert additives, such as emulsifiers or dispersants, with the formulations.

Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, for example ligno-, phenol-, naphthalene- and dibutyl-naphthalenesulfonic acids, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, or of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctyl-, octyl-, or nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether

alcohols, triisodecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, liginosulfite waste liquors or methyl cellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or jointly grinding fungicides A) and B) and optionally pesticide C) or the mixture of the fungicides A) and B) and pesticide C) with a solid carrier.

Granules (for example coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active compound, or active compounds, to a solid carrier.

Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicic acids, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, and fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

The percentage of fungicides in the formulation depends on the type of formulation. According to a specific embodiment of the invention, liquid formulations are prepared to comprise 5% to 50% (calculated based on active ingredients' content) of fungicides A) and B) and may optionally further contain up to 30% of insecticide C) (calculated based on

active ingredients' content). Solid formulations such as powders and granules comprise 40% to 98% of fungicides A) and B) (calculated based on active ingredients' content) and may optionally further contain up to 30% of insecticide C) (calculated based on active ingredients' content). The weight ratio in the formulations between the active ingredients of fungicides A) and B) are from 1:10 to 10:1.

In yet a specific preferred embodiment of the present invention the fungicidal composition is formulated in a water dispersible granule (WDG), suspension concentrate (SC), emulsion in water (EW).

In addition the fungicidal composition may be formulated to further contain solvents, adjuvants and excipients, all known to the skilled artisan.

The present invention further provides a tank-mix comprising a combination of fungicide A) and B) and optionally pesticide C). The tank mix is prepared according to methods well known to the skilled person, including mixing at least one formulation selected according to the desired treatment in a large tank suitable for application. Instructions for preparing tank mixes, comprising fungicides A) and B) and optionally pesticide C), are provided on the commercial products' label. However, the synergistic effect is achieved by preparing the tank mix with 80% or less of the recommended quantity of the commercial product.

According to a specific embodiment of the invention the tank mix is prepared by mixing the components which are fungicide A) selected from Calirus 150 or Calirus 980 with

at least one fungicide B) and optionally at least one pesticide C) in accordance with the preparation instructions and dose/rate recommendations on the commercial products' labels. In the preparation of the tank mix, the required amounts of components can be adjusted in order to achieve the synergistic effect in accordance with the presently claimed method. E.g. using 80% or less of the recommended amounts as recommended on the label of the commercially available products, wherein said recommendation refers to the use of only the individual component.

The compositions, tank mixes and method of the present invention are effective in the control of phytopathogenic fungi and plant diseases. Non-limiting examples of phytopathogenic fungi are fungi belonging to the following classes: Ascomycetes (e.g. *Venturia*, *Podosphaera*, *Erysiphe*, *Monilinia*, *Mycosphaerella*, *Uncinula*); Basidiomycetes (e.g. the genus *Hemileia*, *Rhizoctonia*, *Phakopsora*, *Puccinia*, *Ustilago*, *Tilletia*); Fungi imperfecti (also known as Deuteromycetes; e.g. *Botrytis*, *Helminthosporium*, *Rhynchosporium*, *Fusarium*, *Septoria*, *Cercospora*, *Alternaria*, *Pyricularia* and *Pseudocercospora*); Oomycetes (e.g. *Phytophthora*, *Peronospora*, *Pseudoperonospora*, *Albugo*, *Bremia*, *Pythium*, *Pseudosclerospora*, *Plasmopara*); rust, sigatoka, powdery scub, club root and sclerotinia.

The compositions, tank mix and methods of the present invention are effective in controlling phytopathogenic fungi in the following species of plants: grape vines; cereals, such as wheat, barley, rice, rye or oats; beet, such as sugar beet or fodder beet; fruits, such as pomes,

stone fruits or soft fruits, for example apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries or blackberries; leguminous plants, such as beans, lentils, peas or soybeans; oil plants, such as rape, mustard, poppy, olives, sunflowers, coconut, palm, castor oil plants, cocoa beans or groundnuts; cucumber plants, such as marrows, cucumbers or melons; fiber plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceae, such as avocados, cinnamon or camphor; maize; tobacco; nuts; coffee; sugar cane; tea; vines; hops; durian; papaya, bananas; natural rubber plants; turf or ornamentals, such as flowers, shrubs, broad-leaved trees or evergreens, for example conifers. This list does not represent any limitation.

While embodiments of the invention have been described by way of illustration, it will be apparent that the invention may be carried out with many modifications, variations and adaptations, without departing from its spirit or exceeding the scope of the claims.

It should be understood that some modification, alteration and substitution is anticipated and expected from those skilled in the art without departing from the teachings of the invention. Accordingly, it is appropriate that the following claims be construed broadly and in a manner consistent with the scope and spirit of the invention.

CLAIMS

1. A method for controlling plant pathogens, said method comprising applying to a plant, to a plant locus or to a plant propagation material a combination of fungicides A) and B) wherein fungicide A) is a metal-containing fungicidal composition said metal comprising a mixture of zinc and copper, and B) is an organic fungicide-containing composition, said combination of fungicides optionally further comprising a pesticidal component C) which is an insecticide or a mixture thereof.
2. A method according to claim 1, wherein fungicide A) comprises (a) zinc and copper metal ions; (b) one or more chelating agents selected from the group consisting of citric acid, citrates, and mixtures thereof; and (c) phosphorous acid, and/or salt or hydrate thereof.
3. A method according to claims 1 to 2 wherein fungicide B) comprises at least one fungicide selected from the group consisting of strobilurin fungicides; azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, trifloxystrobin, cyzofamid; azole fungicides; azaconazole, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole, pefurazoate, penconazole, prochloraz, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol,

triflumizole, triticonazole, diclobutrazol, etaconazole, furconazole, furconazole-cis and quinconazole; phenyl pyrrole fungicides; fenpiclonil and fludioxonil; anilino-pyrimidine fungicides; as cyprodinil, mepanipyrim and pyrimethanil; morpholine fungicides; aldimorph, dimethimorph, dodemorph, fenpropimorph, tridemorph, fenpropidin, spiroxamine; piperalin, chlorothalonil; famoxadone; fenamidone; benalaxyl; benalaxyl-M; benomyl; bitertanol; boscalid; carboxin; carpropamid; copper (diverse salts); copper ammoniumcarbonate; copper octanoate; copper oleate; copper sulphate; copper hydroxide; captan, cyazofamid; cymoxanil; diethofencarb; dithianon; fenhexamide; fenoxycarb; fluazinam; flutolanil; folpet; fosetyl-Al, guazatine; hymexazole; iprodione; mancozeb; metalaxyl; mefenoxam; metrafenone; nuarimol; paclobutrazol; pencycuron; penthiopyrad; procymidone; pyroquilon; quinoxifen; silthiofam; sulfur; thiabendazole; thiram; triazoxide; tricyclazole; proquinazid; captan; trinexapac-ethyl; chlormequat chloride; ethephon; and acibenzolar-5-methyl; mineral oils and formulations thereof with pesticidal activity, e.g. Enspray™ 99 by SK; and essential oils and formulations thereof, e.g. tea tree oil, Timorex™, and Timorex™ Gold.

4. A method according to claims 1 to 3 wherein said insecticide is selected from the group consisting of carbamate, macrocyclic lactone, neonicotinoid and pyrethroid insecticides; carbofuran, carbosulfan, abamectin, emamectin, spinosad, imadacloprid, dinotefuran, thiamethoxam, acetamiprid, thiacloprid, chloropyrifos, fipronil, indoxacarb, bifenthrin,

cyfluthrin, lambda-cyhalothrin, cypermethrin, zeta-cypermethrin, deltamethrin, tau-fluvalinate, and mixtures thereof.

5. A method according to claims 1 to 4 wherein fungicides A) and B) are applied at a total dose/rate which is 80% or less than the dose/rate recommended on the commercial fungicidal product label of the individual products.
6. A method according to claims 1 to 5 comprising applying to plant propagation materials or locus of planting or sowing, a combination of fungicides A) and B) and optionally a pesticide C).
7. A method according to claim 6 wherein the crop and/or plants treated are treated at application rates of 0.1 to 10,000 g/ha, preferably 10 to 1,000 g/ha.
8. A method according to claim 6 wherein the plant propagation materials are seeds, and the application rates of the combination are between 0.001 and 50 g per kilogram of seed, preferably between 0.01 and 10 g per kilogram of seed.
9. A method according to claim 6 wherein the locus is soil and the application rates of the combination are between 0.1 and 10 000 g/ha, preferably between 1 and 5 000 g/ha.
10. A method according to claims 1 to 9 wherein the application of the fungicides is carried out by separate, sequential or simultaneous application doses.

11. A method according to claim 6 wherein the application of the fungicides and insecticide is carried out by separate, sequential or simultaneous application doses.
12. A synergistic fungicidal composition comprising a combination of fungicides A) and B) wherein fungicide A) is a metal-containing fungicidal composition said metal comprising a mixture of zinc and copper, and B) is an organic fungicide-containing composition, said combination of fungicides optionally further comprising a pesticidal component C) which is an insecticide or mixture thereof.
13. A synergistic composition according to claim 12, formulated in the form of ready-to-spray solutions, powders and suspensions, or in the form of highly concentrated aqueous, oily or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, the formulations being applied by spraying, atomizing, dusting, broadcasting or watering.
14. A synergistic composition according to claim 13 wherein said formulations are selected from among EC (Emulsifiable Concentrate), WP (Wettable Powder), SL (Soluble Liquid concentrate), SP (Soluble Powder), SC (Suspension Concentrate), CS (Capsule Suspensions) and WG (Water Dispersible Granules).
15. A synergistic composition according to claims 12 to 14 wherein the content of fungicides A) and B) in the

formulations is from 5% to 50% (based on active ingredients' content), and the content of insecticide C) is up to 30% (based on active ingredients' content) when said formulations are in liquid form.

16. A synergistic composition according to claims 12 to 14 comprising 40% to 98% of fungicides A) and B) (based on active ingredients' content) and up to 30% of insecticide C) (based on active ingredients' content) wherein said formulations are in solid form.
17. A synergistic composition according to claims 12 to 14 wherein the weight ratio in the formulations between the active ingredients of fungicides A) and B) is from 1:10 to 10:1.
18. A synergistic composition according to claims 12 to 17, wherein fungicide A) comprises (a) zinc and copper metal ions; (b) one or more chelating agent selected from the group consisting of citric acid, citrates, and mixtures thereof; and (c) phosphorous acid, and/or salt or hydrate thereof.
19. A synergistic composition according to claims 12 to 18, wherein fungicide B) comprises at least one fungicide selected from a group comprising of strobilurin fungicides; azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, trifloxystrobin, cyzofamid; azole fungicides; azaconazole, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole,

fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole, pefurazoate, penconazole, prochloraz, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole, diclobutrazol, etaconazole, furconazole, furconazole-cis and quinconazole; phenyl pyrrole fungicides; fenpiclonil and fludioxonil; anilino-pyrimidine fungicides; as cyprodinil, mepanipyrim and pyrimethanil; morpholine fungicides; aldimorph, dimethimorph, dodemorph, fenpropimorph, tridemorph, fenpropidin, spiroxamine; piperalin, chlorothalonil; famoxadone; fenamidone; benalaxyl; benalaxyl-M; benomyl; bitertanol; boscalid; carboxin; carpropamid; copper (diverse salts); copper ammoniumcarbonate; copper octanoate; copper oleate; copper sulphate; copper hydroxide; captan, cyazofamid; cymoxanil; diethofencarb; dithianon; fenhexamide; fenoxycarb; fluazinam; flutolanil; folpet; fosetyl-Al, guazatine; hymexazole; iprodione; mancozeb; metalaxyl; mefenoxam; metrafenone; nuarimol; paclobutrazol; pencycuron; penthiopyrad; procymidone; pyroquilon; quinoxifen; silthiofam; sulfur; thiabendazole; thiram; triazoxide; tricyclazole; proquinazid; captan; trinexapac-Ethyl; chlormequat chloride; ethephon; and acibenzolar-5-methyl; mineral oils and formulations thereof with pesticidal activity, e.g. Enspray™ 99 by SK; and essential oils and formulations thereof, e.g. tea tree oil, Timorex™, and Timorex™ Gold.

20. A synergistic composition according to claims 12 to 18, wherein pesticide C) is selected from the group

consisting of carbamate, macrocyclic lactone, neonicotinoid and pyrethroid insecticides; carbofuran, carbosulfan, abamectin, emamectin, spinosad, imadacloprid, dinotefuran, thiamethoxam, acetamiprid, thiacloprid, chloropyrifos, fipronil, indoxacarb, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, zeta-cypermethrin, deltamethrin, tau-fluvalinate, and mixtures thereof.

21. A tank mix containing a combination of fungicides A) and B) wherein fungicide A) is a metal-containing fungicidal composition said metal comprising a mixture of zinc and copper, and B) is an organic fungicide-containing composition, said combination of fungicides optionally further comprising a pesticidal component C) which is an insecticide or a mixture thereof.
22. A tank mix according to claim 21, wherein fungicide A) comprises (a) zinc and copper metal ions; (b) one or more chelating agent selected from the group consisting of citric acid, citrates, and mixtures thereof; and (c) phosphorous acid, and/or salt or hydrate thereof.
23. A tank mix according to claims 21 to 22 wherein fungicide B) is at least one fungicide selected from a group comprising of strobilurin fungicides; azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, trifloxystrobin, cyzofamid; azole fungicides; azaconazole, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole,

flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole, pefurazoate, penconazole, prochloraz, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole, diclobutrazol, etaconazole, furconazole, furconazole-cis and quinconazole; phenyl pyrrole fungicides; fenpiclonil and fludioxonil; anilino-pyrimidine fungicides; as cyprodinil, mepanipyrim and pyrimethanil; morpholine fungicides; aldimorph, dimethimorph, dodemorph, fenpropimorph, tridemorph, fenpropidin, spiroxamine; piperalin, chlorothalonil; famoxadone; fenamidone; benalaxyl; benalaxyl-M; benomyl; bitertanol; boscalid; carboxin; carpropamid; copper (diverse salts); copper ammoniumcarbonate; copper octanoate; copper oleate; copper sulphate; copper hydroxide; captan, cyazofamid; cymoxanil; diethofencarb; dithianon; fenhexamide; fenoxycarb; fluazinam; flutolanil; folpet; fosetyl-Al, guazatine; hymexazole; iprodione; mancozeb; metalaxyl; mefenoxam; metrafenone; nuarimol; paclobutrazol; pencycuron; penthiopyrad; procymidone; pyroquilon; quinoxifen; silthiofam; sulfur; thiabendazole; thiram; triazoxide; tricyclazole; proquinazid; captan; trinexapac-Ethyl; chlormequat chloride; ethephon; and acibenzolar-5-methyl; mineral oils and formulations thereof with pesticidal activity, e.g. Enspray™ 99 by SK; and essential oils and formulations thereof, e.g. tea tree oil, Timorex™, and Timorex™ Gold.

24. A tank mix according to claims 21 to 23 wherein pesticide C) is at least one insecticide wherein said

insecticide is selected from a group comprising carbamate, macrocyclic lactone, neonicotinoid and pyrethroid insecticides; carbofuran, carbosulfan, abamectin, emamectin, spinosad, imadacloprid, dinotefuran, thiamethoxam, acetamiprid, thiacloprid, chloropyrifos, fipronil, indoxacarb, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, zeta-cypermethrin, deltamethrin, tau-fluvalinate and mixtures thereof.

25. A tank mix according to claims 21 to 24 wherein said tank mix is prepared to contain fungicides A) and B) at a total which is 80% or less than the recommended concentration of the commercial fungicidal product label of the individual products.
26. A method according to claims 1 to 11 for the control of phytopathogenic fungi, and plant diseases caused by said fungi, selected from the group consisting of Ascomycetes (Venturia, Podosphaera, Erysiphe, Monilinia, Mycosphaerella, Uncinula); Basidiomycetes (the genus Hemileia, Rhizoctonia, Phakopsora, Puccinia, Ustilago, Tilletia); Fungi imperfecti (also known as Deuteromycetes; Botrytis, Helminthosporium, Rhynchosporium, Fusarium, Septoria, Cercospora, Alternaria, Pyricularia and Pseudocercospora); Oomycetes (Phytophthora, Peronospora, Pseudoperonospora, Albugo, Bremia, Pythium, Pseudosclerospora, Plasmopara); rust, sigatoka, powdery scub, club root, and sclerotinia.

27. A method according to claims 1 to 11, wherein said plant is selected from the group consisting of grape vines; cereals; wheat, barley, rice, rye or oats; beets; sugar beet or fodder beets; fruits; pomes, stone fruits or soft fruits (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries or blackberries; leguminous plants; beans, lentils, peas or soybeans; oil plants; rape, mustard, poppy, olives, sunflowers, coconut, palm, castor oil plants, cocoa beans or groundnuts; cucumber plants; marrows, cucumbers or melons; fiber plants; cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or mandarins; vegetables; spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceae; avocados, cinnamon or camphor; maize; tobacco; nuts; coffee; sugar cane; tea; vines; hops; durian; papaya, bananas; natural rubber plants; turf or ornamentals; flowers, shrubs, broad-leaved trees or evergreens; and conifers.
28. A composition according to claims 12 to 20 for the control of phytopathogenic fungi and plant diseases selected from a group comprising phytopathogenic fungi which are fungi belonging to the following classes: Ascomycetes (Venturia, Podosphaera, Erysiphe, Monilinia, Mycosphaerella, Uncinula); Basidiomycetes (the genus Hemileia, Rhizoctonia, Phakopsora, Puccinia, Ustilago, Tilletia); Fungi imperfecti (also known as Deuteromycetes; Botrytis, Helminthosporium, Rhynchosporium, Fusarium, Septoria, Cercospora, Alternaria, Pyricularia and Pseudocercospora); Oomycetes (Phytophthora, Peronospora, Pseudoperonospora,

Albugo, Bremia, Pythium, Pseudosclerospora, Plasmopara).
Rust, sigatoga, powdery scub, club root and scelrotinia.

29. A composition according to claim 12 to 20 for the control of phytopathogenic fungi in the following species of plants: grape vines; cereals; wheat, barley, rice, rye or oats; beets; sugar beet or fodder beets; fruits; pomes, stone fruits or soft fruits (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries or blackberries; leguminous plants; beans, lentils, peas or soybeans; oil plants; rape, mustard, poppy, olives, sunflowers, coconut, palm, castor oil plants, cocoa beans or groundnuts; cucumber plants; marrows, cucumbers or melons; fiber plants; cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or mandarins; vegetables; spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceae; avocados, cinnamon or camphor; maize; tobacco; nuts; coffee; sugar cane; tea; vines; hops; durian; papaya, bananas; natural rubber plants; turf or ornamentals; flowers, shrubs, broad-leaved trees or evergreens; conifers.

30. A tank mix according to claims 21 to 25 for the control of phytopathogenic fungi and plant diseases selected from a group comprising phytopathogenic fungi which are fungi belonging to the following classes: Ascomycetes (Venturia, Podosphaera, Erysiphe, Monilinia, Mycosphaerella, Uncinula); Basidiomycetes (the genus Hemileia, Rhizoctonia, Phakopsora, Puccinia, Ustilago, Tilletia); Fungi imperfecti (also known as Deuteromycetes; Botrytis, Helminthosporium,

Rhynchosporium, Fusarium, Septoria, Cercospora, Alternaria, Pyricularia and Pseudocercospora); Oomycetes (Phytophthora, Peronospora, Pseudoperonospora, Albugo, Bremia, Pythium, Pseudosclerospora, Plasmopara); rust, sigatoga, powdery scub, club root and sclerotinia.

31. A tank mix according to claims 21 to 25 for the control of phytopathogenic fungi in the following species of plants: grape vines; cereals; wheat, barley, rice, rye or oats; beets; sugar beet or fodder beets; fruits; pomes, stone fruits or soft fruits (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries or blackberries; leguminous plants; beans, lentils, peas or soybeans; oil plants; rape, mustard, poppy, olives, sunflowers, coconut, palm, castor oil plants, cocoa beans or groundnuts; cucumber plants; marrows, cucumbers or melons; fiber plants; cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or mandarins; vegetables; spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceae; avocados, cinnamon or camphor; maize; tobacco; nuts; coffee; sugar cane; tea; vines; hops; durian; papaya, bananas; natural rubber plants; turf or ornamentals; flowers, shrubs, broad-leaved trees or evergreens; conifers.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2017/050676

A. CLASSIFICATION OF SUBJECT MATTER

IPC (2017.01) A01N 25/00, A01N 59/16, A01N 59/20, A01N 57/26, A01N 37/04

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)

IPC (2017.01) A01N 25/00, A01N 59/16, A01N 59/20, A01N 59/26

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

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

Databases consulted: Esp@cenet, Google Patents, PatBase

Search terms used: zinc, copper, metal, citric acid, chelate, phosphorous acid, fungicide, insecticide, synergist

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2914411 A1 BASF SE [DE] 24 Dec 2014 (2014/12/24) abstract, p.5, lines 36-39, p. 18, lines 23-25, p. 8, lines 8-9, p. 7, lines 38-40, p. 53, line 27, p. 51-53, p.57, p. 91 lines 41-43, p. 92 lines 6-16, p. 81, lines 3-8, p. 82, lines 2-17, claim 15, p. 88, lines 7-14, p. 93, lines 5-13, p. 50 lines 3-7	1-31
X	WO 2009082206 A1 CERADIS BV [NL]; VAN DER KRIEKEN WIM [NL]; KOK HANS [NL]; DAVELAAR EVERT [NL]; STEVENS LUC [NL] 02 Jul 2009 (2009/07/02) summary of invention, p. 3 lines 20-26, example 4	1-31

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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Information on patent family members

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