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(54) Title: FUNGICIDAL COMPOSITIONS

(57) Abrégé/Abstract:
The invention relates to a composition capable of controlling phytopathogenic fungi on a plant or propagation material thereof said composition comprising as active ingredients a mixture of: (A) Difenoconazole or a salt or metal complex thereof; and (B) Chlorothalonil, wherein said Difenoconazole or the salt or metal complex thereof and said Chlorothalonil are present in said composition in amounts which produce a synergistic effect. The composition of the invention is also suitable for the protection of industrial materials.

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(54) Title: FUNGICIDAL COMPOSITIONS

(57) Abstract: The invention relates to a composition capable of controlling phytopathogenic fungi on a plant or propagation material thereof said composition comprising as active ingredients a mixture of: (A) Difenoconazole or a salt or metal complex thereof; and (B) Chlorothalonil, wherein said Difenoconazole or the salt or metal complex thereof and said Chlorothalonil are present in said composition in amounts which produce a synergistic effect. The composition of the invention is also suitable for the protection of industrial materials.

FUNGICIDAL COMPOSITIONS

The present invention relates to novel fungicidal compositions capable of controlling phytopathogenic fungi on plants and to a method of controlling such fungi on plants.

Difenoconazole (1-[2-[2-chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole) is a fungicide which is effective against a number of diseases caused by *Ascomycetes*, *Basidiomycetes* and *Deuteromycetes*. Chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) is a fungicide which is effective against *Ascomycetes* and *Deuteromycetes*.

Crop tolerance and activity against phytopathogenic plant fungi of both fungicides does not always satisfy the needs of agricultural practice in many incidents and aspects.

Out of the above-mentioned needs of agricultural practice for increased crop tolerance and/or increased activity against phytopathogenic plant fungi, the present invention seeks to provide a composition which does not suffer from the drawbacks of the prior art.

According to the present invention there is provided a composition capable of controlling phytopathogenic fungi on a plant or propagation material thereof said composition comprising as active ingredients a mixture of: (A) Difenoconazole or a salt or metal complex thereof; and (B) Chlorothalonil, wherein said Difenoconazole or the salt or metal complex thereof and said Chlorothalonil are present in said composition in amounts which produce a synergistic effect.

It has now been found, surprisingly, that the mixture of component (A) and component (B) not only brings about the enhancement of the spectrum of action with respect to the phytopathogen to be controlled but achieves a synergistic effect which extends the range of action of component (A) and component (B) in two ways. Firstly, the rates of application of component (A) and component (B) are lowered whilst the action remains equally good. Secondly, the active ingredient mixture still achieves a high degree of phytopathogen control even where the two individual components have become totally ineffective in such a low application rate range. This allows, on the one hand, a substantial broadening of the

spectrum of phytopathogens that can be controlled and, on the other hand, increased safety in use.

However, besides the actual synergistic action with respect to fungicidal activity, the pesticidal compositions according to the invention can also have further surprising advantageous properties which can also be described, in a wider sense, as synergistic activity. Examples of such advantageous properties that may be mentioned are: a broadening of the spectrum of fungicidal activity to other phytopathogens, for example to resistant strains; a reduction in the rate of application of the active ingredients; more advantageuos degradability; improved toxicological and/or ecotoxicological behaviour; or improved characteristics of the plants including: emergence, crop yields, more developed root system, tillering increase, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf colour, less fertilizers needed, less seeds needed, more productive tillers, earlier flowering, early grain maturity, less plant verse (lodging), increased shoot growth, improved plant vigor, and early germination.

Difenoconazole and Chlorothalonil are described in „The Pesticide Manual" [The Pesticide Manual - A World Compendium; Thirteenth Edition; Editor: C. D. S. Tomlin; The British Crop Protection Council]. Difenoconazole is described therein under the entry number 247 and Chlorothalonil is described under entry number (142).

Difenoconazole can exist in different stereoisomeric forms. The invention covers mixtures comprising all those stereoisomeric forms or mixtures of those stereoisomeric forms in any ratio.

The mentioned salts of Difenoconazole can be prepared by reacting the respective free form of Difenoconazole with acids.

Of the acids that can be used for the preparation of salts of Difenoconazole, the following may be mentioned: hydrohalic acids, such as hydrofluoric acid, hydrochloric acid, hydrobromic acid or hydriodic acid; sulfuric acid, phosphoric acid, nitric acid, and organic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid, propionic acid, glycolic acid, thiocyanic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic acid, formic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid,

salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid, 2-acetoxybenzoic acid and 1,2-naphthalene-disulfonic acid.

Metal complexes consist of the underlying organic molecule and an inorganic or organic metal salt, for example a halide, nitrate, sulfate, phosphate, acetate, trifluoroacetate, trichloroacetate, propionate, tartrate, sulfonate, salicylate, benzoate, etc., of an element of main group II, such as calcium and magnesium, and of main groups III and IV, such as aluminium, tin or lead, and of subgroups I to VIII, such as chromium, manganese, iron, cobalt, nickel, copper, zinc, etc.. Preference is given to the subgroup elements of the 4th period. The metals may have any of the different valencies in which they occur. The metal complexes can be mono- or poly-nuclear, i.e. they can contain one or more organic molecule components as ligands.

In one embodiment of the invention, component (A) is Difenoconazole in the free form.

Throughout this document the expression “composition” stands for the various mixtures or combinations of component (A) and component (B), for example in a single “ready-mix” form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a “tank-mix”, and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying component (A) and component (B) is not essential for working the present invention.

The compositions according to the invention may also comprise additional pesticides.

The compositions according to the invention are effective against harmful microorganisms, such as microorganisms, that cause phytopathogenic diseases, in particular against phytopathogenic fungi and bacteria.

The compositions according to the invention are effective especially against phytopathogenic 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 Pseudocercosporella); *Oomycetes* (e.g. *Phytophthora, Peronospora, Pseudoperonospora, Albugo, Bremia, Pythium, Pseudosclerospora, Plasmopara*).

Throughout this specification the term "plant"/"plants" includes plants of the following species: grape vines; cereals, such as wheat, barley, 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, castor oil plants, cocoa beans or groundnuts; cucumber plants, such as marrows, cucumbers or melons; fibre 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; bananas; natural rubber plants; turf or ornamentals, such as flowers, shrubs, broad-leaved trees or evergreens, for example conifers.

More specifically, "plant"/"plants" of particular interest in connection with present invention are cereals; soybean; rice; oil seed rape; pome fruits; stone fruits; peanuts; coffee; tea; strawberries; turf; vines and vegetables, such as tomatoes, potatoes, cucurbits and lettuce.

The term "plant"/"plants" also includes genetically modified plants including those plants which have been rendered resistant to herbicides, insecticides, fungicides or have been modified in some other way such as to enhance yield, drought tolerance or quality. Such genetically modified plants may have been modified via recombinant nucleic acid techniques well know to the person skilled in the art.

The term "plant propagation material" is understood to denote generative parts of a plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected before transplantation by a total or partial treatment by immersion.

In a particular embodiment "plant propagation material" means seeds.

The compositions according to the invention are particularly effective against powdery mildews; rusts; leafspot species; early blights and molds; especially against *Septoria, Puccinia, Erysiphe, Pyrenophora, Fusarium* and/or *Tapesia* in cereals; *Phakopsora* in soybeans; *Hemileia* in coffee; *Phragmidium* in roses; *Alternaria* in potatoes, tomatoes and cucurbits; *Sclerotinia* in turf, vegetables, sunflower and oil seed rape; black rot, red fire, powdery mildew, grey mold and dead arm disease in vine; *Botrytis cinerea* in fruits; *Monilinia spp.* in fruits.

The compositions according to the invention are particularly useful for controlling the following plant diseases:
Alternaria species in fruit and vegetables,
Ascochyta species in pulse crops,
Botrytis cinerea in strawberries, tomatoes, sunflower, pulse crops, vegetables and grapes,
Cercospora arachidicola in peanuts,
Cochliobolus sativus in cereals,
Colletotrichum species in pulse crops,
Erysiphe species in cereals,
Erysiphe cichoracearum and *Sphaerotheca fuliginea* in cucurbits,
Fusarium species in cereals and maize,
Gäumannomyces graminis in cereals and lawns,
Helminthosporium species in maize, rice and potatoes,
Hemileia vastatrix on coffee,
Microdochium species in wheat and rye,
Phakopsora species in soybean,
Puccinia species in cereals, broadleaf crops and perrenial plants,
Pseudocercosporella species in cereals,
Phragmidium mucronatum in roses,
Podosphaera species in fruits,
Pyrenophora species in barley,
Pyricularia oryzae in rice,
Ramularia collo-cygni in barley,

Rhizoctonia species in cotton, soybean, cereals, maize, potatoes, rice and lawns,
Rhynchosporium secalis in barley and rye,
Sclerotinia species in lawns, lettuce, vegetables and oil seed rape,
Septoria species in cereals, soybean and vegetables,
Sphacelotheca reilliana in maize,
Tilletia species in cereals,
Uncinula necator, *Guignardia bidwellii* and *Phomopsis viticola* in vines,
Urocystis occulta in rye,
Ustilago species in cereals and maize,
*Venturi*a species in fruits,
Monilinia species on fruits,
Mycosphaerella fijiensis on banana.

The amount of a composition according to the invention to be applied, will depend on various factors, such as the compounds employed; the subject of the treatment, such as, for example plants, soil or seeds; the type of treatment, such as, for example spraying, dusting or seed dressing; the purpose of the treatment, such as, for example prophylactic or therapeutic; the type of fungi to be controlled or the application time.

The present invention further provides a composition as described above wherein the weight ratio of said Difenoconazole or the salt or metal complex thereof to said Chlorothalonil is from 2000 : 1 to 1 : 1000.

It has been found that the use of component (B), namely Chlorothalonil, in combination with component (A), namely Difenoconazole, surprisingly and substantially enhances the effectiveness of the latter against fungi, and vice versa. Additionally, the method of the invention is effective against a wider spectrum of such fungi that can be combated with the active ingredients of this method, when used solely.

The weight ratio of component (A) to component (B) is so selected as to give a synergistic activity. In general, as mentioned above, the weight ratio of component (A) to component (B) is from 2000 : 1 to 1 : 1000. In a particular embodiment the weight ratio of component (A) to component (B) is from 100 : 1 to 1: 100. In a further embodiment the weight ratio of component (A) to component (B) is from 20 : 1 to 1: 50.

The synergistic activity of the compositions according to the invention is apparent from the fact that, amongst other things, the fungicidal activity of the composition of component (A) and component (B) is greater than the sum of the fungicidal activities of component (A) and component (B).

The compositions according to the invention have a systemic action and can be used as foliar, soil and seed treatment fungicides.

With the compositions according to the invention it is possible to inhibit or destroy the phytopathogenic microorganisms which occur in plants or in parts of plants (fruit, blossoms, leaves, stems, tubers, roots), while at the same time the parts of plants which grow later are also protected from attack by phytopathogenic microorganisms.

The compositions according to the invention are of particular interest for controlling a large number of fungi in various plants or their seeds, especially in field crops such as potatoes, tobacco and sugarbeets, and wheat, rye, barley, oats, rice, maize, lawns, cotton, soybeans, oil seed rape, pulse crops, sunflower, coffee, sugarcane, fruit and ornamentals in horticulture and viticulture, in vegetables such as cucumbers, beans and cucurbits.

The compositions according to the invention are applied by treating the fungi, the plants or the propagation material thereof with a composition according to the invention.

The compositions according to the invention may be applied before or after infection of the plants or the propagation material thereof by the fungi.

When applied to the plants component (A) is applied at a rate of 5 to 2000 g a.i./ha, particularly 10 to 1000 g a.i./ha, e.g. 50, 75, 100 or 200 g a.i./ha, in association with 1 to 5000 g a.i./ha, particularly 2 to 2000 g a.i./ha, e.g. 100, 250, 500, 800, 1000, 1500 g a.i./ha of component (B).

In agricultural practice the application rates of the compositions according to the invention depend on the type of effect desired, and typically range from 20 to 4000 g of total composition per hectare.

When the compositions according to the invention are used for treating seed, rates of 0.001 to 50 g of component (A) per kg of seed, particularly from 0.01 to 10g per kg of seed, and 0.001 to 50 g of component (B), per kg of seed, particularly from 0.01 to 10g per kg of seed, are generally sufficient.

The composition of the invention may be employed in any conventional form, for example in the form of a twin pack, a powder for dry seed treatment (DS), an emulsion for seed treatment (ES), a flowable concentrate for seed treatment (FS), a solution for seed treatment (LS), a water dispersible powder for seed treatment (WS), a capsule suspension for seed treatment (CF), a gel for seed treatment (GF), an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), an emulsion, water in oil (EO), an emulsion, oil in water (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a technical concentrate (TK), a dispersible concentrate (DC), a wettable powder (WP) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

Such compositions may be produced in conventional manner, e.g. by mixing the active ingredients with appropriate inert formulation adjuvants (diluents, solvents, fillers and optionally other formulating ingredients such as surfactants, biocides, anti-freeze, stickers, thickeners and compounds that provide adjuvancy effects). Also conventional slow release formulations may be employed where long lasting efficacy is intended. Particularly formulations to be applied in spraying forms, such as water dispersible concentrates (e.g. EC, SC, DC, OD, SE, EW, EO and the like), wettable powders and granules, may contain surfactants such as wetting and dispersing agents and other compounds that provide adjuvancy effects, e.g. the condensation product of formaldehyde with naphthalene sulphonate, an alkylarylsulphonate, a lignin sulphonate, a fatty alkyl sulphate, and ethoxylated alkylphenol and an ethoxylated fatty alcohol.

A seed dressing formulation is applied in a manner known per se to the seeds employing the compositions according to the invention and a diluent in suitable seed dressing formulation form, e.g. as an aqueous suspension or in a dry powder form having good adherence to the

seeds. Such seed dressing formulations are known in the art. Seed dressing formulations may contain the single active ingredients or the combination of active ingredients in encapsulated form, e.g. as slow release capsules or microcapsules.

In general, the formulations include from 0.01 to 90% by weight of active agent, from 0 to 20% agriculturally acceptable surfactant and 10 to 99.99% solid or liquid formulation inerts and adjuvant(s), the active agent consisting of at least component (A) together with component (B), and optionally other active agents, particularly microbiocides or conservatives or the like. Concentrated forms of compositions generally contain in between about 2 and 80%, preferably between about 5 and 70% by weight of active agent. Application forms of formulation may for example contain from 0.01 to 20% by weight, preferably from 0.01 to 5% by weight of active agent. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ diluted formulations.

In a further aspect of the invention there is provided a method of controlling phytopathogenic fungi on a plant or propagation material thereof, which comprises applying to said plant or said propagation material thereof a composition as described above. The method of application, such as spraying, atomising, dusting, scattering, coating or pouring can be chosen in accordance with the prevailing circumstances.

In a particular embodiment of the invention said plant is a cereal plant.

In a still further aspect of the invention there is provided the use of a composition as described above in the prevention and/or treatment of growth and/or infestation of phytopathogenic fungi on a plant.

In a still further aspect of the invention there is provided the use of a composition as described above for the protection of industrial materials. In a particular embodiment said industrial material is selected from the group consisting of: wood; plastic; wood plastic composite; paint; paper; and wallboards.

Industrial material means those materials used for construction and the like. In particular, industrial material includes structural timber, doors, cupboards, storage units, carpets, particularly natural fibre carpets such as wool and hessian, paints, plastics, wood (including

engineered wood) and wood plastic composite. In addition to this, industrial material includes adhesives, sealants, joining materials and joints and insulation material. In a particular embodiment "industrial material" means structural timber. In a further embodiment "industrial material" means engineered wood. In a further embodiment "industrial material" means plastic.

Plastics includes plastic polymers and copolymers, including: acrylonitrile butadiene styrene, butyl rubber, epoxies, fluoropolymers, isoprene, nylons, polyethylene, polyurethane, polypropylene, polyvinyl chloride, polystyrene, polycarbonate, polyvinylidene fluoride, polyacrylate, polymethyl methacrylate, polyurethane, polybutylene, polybutylene terephthalate, polyether sulfone, polyphenyllenoxide, polyphenylene ether, polyphenylene sulfide, polyphtatamide, polysulphene, polyester, silicone, styrene butadiene rubber and combinations of polymers. In a further embodiment "industrial material" means polyvinyl chloride (PVC). In a further embodiment "industrial material" means polyurethane (PU). In a further embodiment "industrial material" means paint. In a further embodiment "industrial material" means wood plastic composite (WPC). Wood plastic composite is a material that is well known in the art. A review of WPCs can be found in the following publication - Craig Clemons - Forrest Products Journal. June 2002 Vol 52. No. 6. pp 10-18.

"Wood" is to be understood as meaning wood and wood products, for example: derived timber products, lumber, plywood, chipboard, flakeboard, laminated beams, oriented strandboard, hardboard, and particleboard, tropical wood, structural timber, wooden beams, railway sleepers, components of bridges, jetties, vehicles made of wood, boxes, pallets, containers, telegraph-poles, wooden fences, wooden lagging, windows and doors made of wood, plywood, chipboard, joinery, or wooden products which are used, quite generally, for building houses or decks, in building joinery or wood products that are generally used in house-building including engineered wood, construction and carpentry.

"Industrial material" also includes cooling lubricants and cooling and heating systems, ventilation and air conditioning systems and parts of production plants, for example cooling-water circuits.

The methods of the invention can be used in the prevention and/or treatment of the growth/infestation by/of a fungus as described within this specification. The fungus can be

controlled by treating the fungus or the industrial material with a composition according to the invention in a convenient manner. Examples of ways in which the fungus or industrial material can be treated with a fungicide according to the invention are: by including said fungicide in the industrial material itself, absorbing, impregnating, treating (in closed pressure or vacuum systems) said material with said fungicide, dipping or soaking the industrial material, or coating the industrial material for example by curtain coating, roller, brush, spray, atomisation, dusting, scattering or pouring application.

In a still further aspect of the invention there is provided Industrial materials comprising a composition as described above. In a particular embodiment said Industrial materials are selected from the group consisting of: wood; plastic; wood plastic composite; paint; paper; and wallboards.

The invention will now be described further with reference to the following non-limiting examples:

Througout the examples the term "active ingredient" denotes a mixture of Difenoconazole (component A) and Chlorothalonil (component B) in a specific mixing ratio.

Formulation Examples

Wettable powders	a)	b)	c)
active ingredient [A): B) = 1:3(a), 1:2(b), 1:1(c)]	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutylnaphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders that can be diluted with water to give suspensions of the desired concentration.

Powders for dry seed treatment	a)	b)	c)
active ingredient [A) : B) = 1:3(a), 1:2(b), 1:1(c)]	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-
Talcum	-	20	

The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording powders that can be used directly for seed treatment.

Emulsifiable concentrate	
active ingredient (A): B) = 1:6)	10 %
octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (35 mol of ethylene oxide)	4 %
Cyclohexanone	30 %
xylene mixture	50 %

Emulsions of any required dilution, which can be used in plant protection, can be obtained from this concentrate by dilution with water.

Dusts	a)	b)	c)
Active ingredient [A) : B) = 1:6(a), 1:2(b), 1:10(c)]	5 %	6 %	4 %
Talcum	95 %	-	-
Kaolin	-	94 %	-
mineral filler	-	-	96 %

Ready-for-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill. Such powders can also be used for dry dressings for seed.

Extruder granules	
Active ingredient (A) : B) = 2:1)	15 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
Kaolin	82 %

The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

Coated granules

Active ingredient (A) : B) = 1:10)	8 %
polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

The finely ground active ingredient is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

Suspension concentrate

active ingredient (A) : B) = 1:8)	40 %
propylene glycol	10 %
nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6 %
Sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
silicone oil (in the form of a 75 % emulsion in water)	1 %
Water	32 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

Flowable concentrate for seed treatment

active ingredient (A) : B) = 1:8)	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
tristyrenephenole with 10-20 moles EO	2 %
1,2-benzisothiazolin-3-one (in the form of a 20% solution in water)	0.5 %
monoazo-pigment calcium salt	5 %
Silicone oil (in the form of a 75 % emulsion in water)	0.2 %
Water	45.3 %

The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

Slow Release Capsule Suspension

28 parts of a combination of cyprodinil and a compound of component B), or of each of these compounds separately, are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of 1.2 parts of polyvinylalcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed.

The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns.

The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

Biological Examples

A synergistic effect exists whenever the action of an active ingredient combination is greater than the sum of the actions of the individual components.

The action to be expected E for a given active ingredient combination obeys the so-called COLBY formula and can be calculated as follows (COLBY, S.R. "Calculating synergistic and antagonistic responses of herbicide combination". Weeds, Vol. 15, pages 20-22; 1967):

ppm = milligrams of active ingredient (= a.i.) per liter of spray mixture

X = % action by active ingredient A) using p ppm of active ingredient

Y = % action by active ingredient B) using q ppm of active ingredient.

According to COLBY, the expected (additive) action of active ingredients A)+B) using p+q ppm of active ingredient is $E = X + Y - \frac{X \cdot Y}{100}$

If the action actually observed (O) is greater than the expected action (E), then the action of the combination is super-additive, i.e. there is a synergistic effect. In mathematical terms the synergism factor SF corresponds to O/E. In the agricultural practice an SF of ≥1.2 indicates significant improvement over the purely complementary addition of activities (expected activity), while an SF of ≤0.9 in the practical application routine signals a loss of activity compared to the expected activity.

Example B-1: Action against Botrytis cinerea on grapes

a) Fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 48-72hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the grape plants are inoculated by spraying a spore suspension ($1x10^6$ conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95% relative humidity in a greenhouse the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-2: Action against Septoria tritici on wheat

a) Fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 72 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment

2 week old wheat plants cv. Riband are treated with the formulated test compound (0.2% active ingredient) in a spray chamber. One day after application, wheat plants are inoculated by spraying a spore suspension ($10x10^5$conidia/ml) on the test plants. After an incubation period of 1 day at 23°C and 95% relative humidity, the plants are kept for 16 days at 23°C and 60% relative humidity in a greenhouse. The disease incidence is assessed 18 days after inoculation. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-3: Action against Pyricularia oryzae on rice

a) Fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 72 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment

Rice leaf segments are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 96 hrs after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-4: Action against Alternaria solani (early blight)

a) Fungal growth assay

Conidia -harvested from a freshly grown colony- of the fungus were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 48 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the tomato plants are inoculated by spraying a spore suspension ($2x10^5$conidia/ml) on the test plants. After an incubation period of 3 days at 20°C and 95% relative humidity in a growth chamber the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-5: Action against Pyrenophora teres (Net blotch)

a) Fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 48 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment

Barley leaf segments are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 96 hrs after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-6: Action against Venturia inaequalis on apple

a) Fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 144 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment

4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the apple plants are inoculated by spraying a spore suspension ($4x10^5$conidia/ml) on the test plants. After an

incubation period of 4 days at 21°C and 95% relative humidity the plants are placed for 4 days at 21°C and 60% relative humidity in a greenhouse. After another 4 day incubation period at 21°C and 95% relative humidity the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-7: Action against Pythium ultimum (Damping off) - fungal growth assay

Mycelial fragments of the fungus, prepared from a fresh liquid culture, were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 48 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-8: Action against Leptosphaeria nodorum (glume blotch) - fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 48 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-9: Action against Pseudocercosporella herpotrichoides var. acuformis (eyespot/cereals) - fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined photometrically after 72 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-10: Action against Ustilago maydis (corn smut) - fungal growth assay

Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined

photometrically after 48 hrs. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-11: Action against Phytophthora infestans (late blight) on tomato – protective treatment

Tomato leaf disks are placed on water agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 96 hrs after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-12: Action against Plasmopara viticola (downy mildew) on grape vines – protective treatment

Grape vine leaf disks are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 7 days after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-13: Action against Botrytis cinerea (Grey mould) on beans – protective treatment

Bean leaf disks are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 96 hrs after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-14: Action against Erysiphe graminis f.sp. hordei (Barley powdery mildew) on barley – protective treatment

Barley leaf segments are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 96 hrs after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-15: Action against Erysiphe graminis f.sp. tritici (Wheat powdery mildew) on barley – protective treatment

Barley leaf segments are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 96 hrs after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-16: Action against Puccinia recondita (Brown rust) on wheat

a) Protective Treatment of leaf segments

Wheat leaf segments are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 9 days after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment of plants

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the wheat plants are inoculated by spraying a spore suspension ($1x10^5$uredospores/ml) on the test plants. After an incubation period of 2 days at 20°C and 95% relative humidity the plants are kept in a greenhouse for 8 days at 20°C and 60% relative humidity. The disease incidence is assessed 10 days after inoculation. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-17: Action against Septoria nodorum on wheat

a) Protective Treatment of leaf segments

Wheat leaf segments are placed on agar in multiwell plates (24-well format) and sprayed with test solutions. After drying, the leaf disks are inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound is assessed 96 hrs after inoculation as preventive fungicidal activity. The fungicide interactions in the combinations are calculated according to COLBY method.

b) Protective Treatment of plants

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the wheat plants are inoculated by spraying a spore suspension ($5x10^5$conidia/ml) on the test plants. After an

incubation period of 1 day at 20°C and 95% relative humidity the plants are kept for 10 days at 20°C and 60% relative humidity in a greenhouse. The disease incidence is assessed 11 days after inoculation. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-18: Action against Podosphaera leucotricha (Powdery mildew) on apple – protective treatment

5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after, the application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12 days at 22°C and 60% relative humidity under a light regime of 14/10hours (light/dark) the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-19: Action against Erysiphe graminis (Powdery mildew) on barley – protective treatment

1 week old barley plants cv. Regina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the barley plants are inoculated by shaking powdery mildew infected plants above the test plants. After an incubation period of 6 days at 20°C / 18°C (day/night) and 60% relative humidity in a greenhouse the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-20: Action against Botrytis cinerea on tomatoes – protective treatment

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the tomato plants are inoculated by spraying a spore suspension ($1x10^5$conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95% relative humidity in a growth chamber the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-21: Action against Helminthosporium teres (Net blotch) on barley – protective treatment

1 week old barley plants cv. Regina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the barley plants are inoculated by spraying a spore suspension ($3x10^4$conidia/ml) on the test plants. After an

incubation period of 4 days at 20°C and 95% relative humditiy in a greenhouse the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

Example B-22: Action against Uncinula necator (Powdery mildew) on grapes – protective treatment

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the grape plants are inoculated by shaking plants infected with grape powdery mildew above the test plants. After an incubation period of 7 days at 26°C and 60% relative humidity under a light regime of 14/10hours (light/dark) the disease incidence is assessed. The fungicide interactions in the combinations are calculated according to COLBY method.

WHAT IS CLAIMED IS:

1. A composition capable of controlling phytopathogenic fungi on a plant or propagation material thereof said composition comprising as active ingredients a mixture of:
(A) Difenoconazole or a salt or metal complex thereof; and
(B) Chlorothalonil,
wherein said Difenoconazole or the salt or metal complex thereof and said Chlorothalonil are present in said composition in amounts which produce a synergistic effect.

2. A composition according to claim 1 wherein the weight ratio of said Difenoconazole or the salt or metal complex thereof to said Chlorothalonil is from 2000 : 1 to 1 : 1000.

3. A method of controlling phytopathogenic fungi on a plant or propagation material thereof, which comprises applying to said plant or said propagation material thereof a composition according to claim 1 or claim 2.

4. A method according to claim 4, wherein said plant is a cereal plant.

5. Use of a composition according to claim 1 or claim 2 in the prevention and/or treatment of growth and/or infestation of phytopathogenic fungi on a plant.

6. Use of a composition according to claim 1 or claim 2 for the protection of industrial materials.

7. Use according to claim 6 wherein said industrial materials are selected from the group consisting of: wood; plastic; wood plastic composite; paint; paper; and wallboards.

8. Industrial materials comprising a composition according to claim 1 or claim 2.

9. Industrial materials according to claim 8 selected from the group consisting of: wood; plastic; wood plastic composite; paint; paper; and wallboards.

10. Industrial materials according to claim 9 wherein said materials comprise wood.