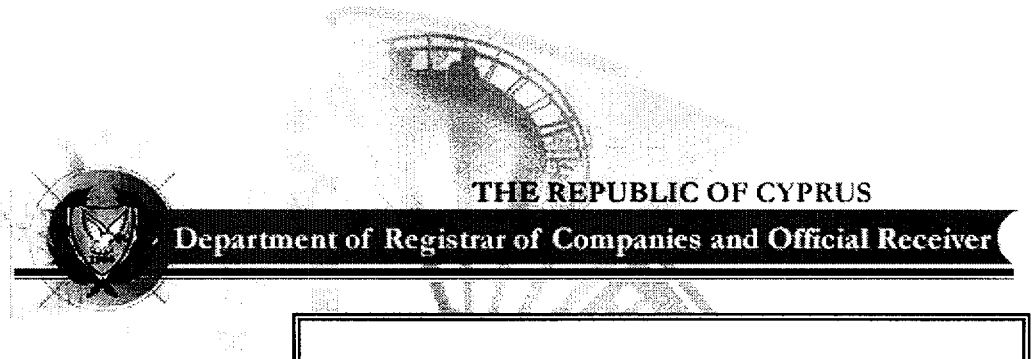

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(54) Fungicidal compositions based on iprodione

(57) New iprodione agricultural fungicidal compositions in fluid form contain

(a) from 20% to 40% of an active ingredient based on iprodione, i.e. 1-isopropylcarbamoyl-3-(3,5-dichlorophenyl)-hydantoin,

(b) an "oil-in-water" emulsion containing from 50% to 160%, relative to the iprodione, of an oil of which the hydrophilic/lipophilic balance (HLB) has a value of 8 to 12 on the scale of HLB values for the preparation of an "oil-in-water" emulsion,

(c) from 0.1% to 2% of a non-ionic emulsifier of the ethylene oxide/fatty alcohol condensate type, and

(d) optionally from 0.5% to 2.5% of a substantially neutral, hydrophilic silica,

the said percentages being by weight. The composition may also contain carbendazime.

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SPECIFICATION

Fungicidal compositions based on iprodione

The present invention relates to new fungicidal compositions based on iprodione.

Iprodione is the well-known name for the agricultural fungicide 1-isopropylcarbamoyl-3-(3,5-dichlorophenyl)-hydantoin. This fungicide has an excellent activity against fungal diseases in plants, in particular botrytis in vines.

Hitherto, this fungicide has been marketed essentially in the form of wettable powder. This formulation has the disadvantage of dispersing dust into the atmosphere when it is handled, either whilst it is being put into bags or whilst the wettable powder is being diluted in water during the preparation of a slurry. Furthermore, this formulation can be washed off the surface of the leaves or seeds in the event of heavy rainfall.

The object of the present invention is to overcome these disadvantages.

The present invention relates to agricultural fungicidal fluid compositions based on iprodione, which contain (the percentages being by weight):

(a) from 20% to 40% of an active ingredient based on iprodione,

(b) an "oil-in-water" emulsion containing 50% to 160%, relative to the iprodione, of an oil of which the hydrophilic-lipophilic balance (HLB) has a value of 8 to 12, and preferably of 10 to 11, on the HLB scale required for the preparation of an "oil-in-water" emulsion,

(c) from 0.1% to 2% of a non-ionic emulsifier of the ethylene oxide/fatty alcohol condensate type, and

(d) optionally from 0.5% to 2.5% of a substantially neutral, hydrophilic silica, the remainder to 100% consisting of water and conventional additives.

The hydrophilic/lipophilic balance is defined and determined according to "Pesticide formulation"—Wade Van Walkenburg—published by Marcel Dekker Inc., New York 1973.

The compositions according to the invention are concentrated suspensions of iprodione in an oil-in-water emulsion. These fluid formulations are frequently referred to in practice as "fluid pastes", "creams" or "flowables".

In these compositions, the active ingredient is based on iprodione in the form of solid particles which have an average diameter of less than 10 microns, and preferably have an average diameter of 1 to 5 microns.

In these suspensions, apart from the iprodione, the active ingredient can include other active substances such as, in particular, carbendazime, benomyl or methyl thiophanate, or a copper-based compound, a metal ethylene-bis-dithiocarbamate such as maneb, zineb or mancozeb, or a phthalimide derivative such as captan, captafol or folpet. However, other mixtures containing iprodione in association with other fungicides can be formulated according to the present invention.

The oil which is used in the compositions according to the invention can be of a variety of types, provided that it can dissolve from 1 to 5 g of iprodione per litre of oil at ordinary temperature, and its hydrophilic/lipophilic balance (HLB) has a value of 8 to 12, and preferably of 10 to 11, on the HLB scale required for the preparation of an "oil-in-water" emulsion; preferably the oil has a viscosity of between 20 and 30 cst.

These oils can be mineral oils such as refined petroleum oils, commonly referred to as white oils, with a boiling range of between 300 and 400°C at atmospheric pressure, and having a high proportion of paraffinic hydrocarbons with, preferably, a minimum proportion of 92% of materials which cannot be sulphonated. Certain vegetable oils, of which the hydrophilic/lipophilic balance has a value within the range specified above, can also be used, such as, for example, groundnut oil, maize germ oil or colza oil.

The ethylene oxide/fatty alcohol condensate emulsifier incorporated in the compositions according to the invention is preferably a condensate of one or more straight- or branched-chain fatty alcohols containing 12 to 14 (preferably 13) carbon atoms with from 8 to 12 mols (preferably from 9 to 10 mols) of ethylene oxide. Such a non-ionic emulsifier provides the stability of the concentrated suspension of iprodione in the oil-in-water emulsion by acting both as a dispersing-wetting agent for the iprodione and as an emulsifier for the binary "oil-water" system.

In certain cases, if it is desired to lessen the amount of oil in order to reduce any possible phytotoxicity, without detracting from the biological properties of the formulation, it can be advantageous to add 0.5% to 2.5% by weight of a preferably substantially neutral, hydrophilic silica to the formulation. In the context of this invention, the term "hydrophilic silica" is to be understood as meaning a silica (preferably synthetic) such as an ultra-fine hydrated precipitated silica with a high specific surface area of the order of 200 to 300 m^2/g, measured according to the B.E.T. method. A silica of this type is substantially neutral, i.e. its pH in aqueous suspension is 7 ± 0.5. In practice, a neutral or weakly acidic silica is preferred.

The compositions according to the invention can also contain conventional adjuvants such as viscosity modifiers (in general from 0.05% to 0.1% by weight) of the polysaccharide type, in particular heteropolysaccharides resulting from the fermentation of carbohydrates by a microorganism of the Xanthomonas type, dispersing-fluidising agents of the ethylene oxide/polyarylphenol condensate type, preferably in the acid phosphate form (in general from 0.5% to 2.5% by weight) anti-freeze agents such

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as ethylene glycol or propylene glycol (in general from 5% to 10% by weight), anti-foam agents such as silicone oil emulsions (generally from 0.2% to 0.6% by weight), and preservatives for combatting microbial proliferations (in general from 0.1% to 0.2% by weight), such as formaldehyde.

The compositions according to the invention can be prepared, for example, in three steps.

The first step consists in preparing the "oil-in-water" emulsion in a tank equipped with a means of vigorous agitation, by running the oil into the water containing the other water-soluble additives and contingently the emulsifier.

In a second step, the iprodione, as a fine powder, is dispersed in the oily emulsion with continued agitation. The suspension obtained is then refined in a mill, e.g. of the ball mill type such as the Dyno-mill.

In the third and final step, the viscosity modifier of the heteropolysaccharide type is dispersed in a small amount of water containing the preservative (e.g. a 40% aqueous solution of formaldehyde) and/or the neutral hydrophilic silica. This dispersion is incorporated into the suspension of iprodione previously obtained.

Apart from having the advantage of being fluid formulations, which are easier to handle than wettable powders, the oily compositions of iprodione according to the invention have the advantage of an enhanced fungicidal efficacy when they are applied in a spraying treatment for combatting fungal diseases in plants (vines, lettuces, tomatoes, strawberry plants, trees bearing small fruits, and the like) and in particular for combatting botrytis (*Botrytis cinerea*) without exhibiting phytotoxicity.

The following Examples illustrate iprodione fluid compositions according to the invention and their preparation.

Example 1

A concentrated oily suspension is prepared which has the following percentage composition by weight:

iprodione with a particle diameter of the order of 2 microns	25.0
paraffinic mineral oil containing more than 70% of paraffin, having a hydrophilic/lipophilic balance with a value of 10.5, and solubilising 1 g of iprodione per litre	33.0
emulsifier based on condensates of 9—10 mols of ethylene oxide with synthetic C_{13} alcohols	0.8
phosphate of ethylene oxide/polystyrylphenol condensate	2.5
ethylene oxide/polyalkylphenol condensate	0.5
ethylene glycol	5.0
heteropolysaccharide (Rhodopol 23)	0.065
formaldehyde (40% aqueous solution)	0.15
silicone oil emulsion	0.5
water q.s.p.	100

Firstly, the water, the glycol, the silicone emulsion and the surface-active agents, including the emulsifier, are mixed in a tank. The mixture is agitated until total dispersion has taken place, and the oil is then run into the mixture.

The iprodione is then added with continued agitation. An emulsion is obtained which is ground in a Dyno-mill to give a concentrated suspension of iprodione.

In the third and final step, the viscosity modifier (heteropolysaccharide), predispersed in a small amount of water containing the preservative (a 40% aqueous formaldehyde solution), is incorporated into the suspension of iprodione to give, finally, a fluid paste or concentrated dispersion which is ready for use.

Example 2

Following the procedure of Example 1, a concentrated oily suspension is prepared which has the following percentage composition by weight:

iprodione	30.0
mineral oil containing more than 70% of paraffin, having a hydrophilic/lipophilic balance with the value of 10, and dissolving 1.2 g of iprodione per litre of oil	20.0
ethylene glycol	5.0
condensates of 8—10 mols of ethylene oxide with synthetic C_{13} alcohols	0.8
acid phosphate of ethylene oxide/polystyrylphenol condensate	1.2
silicone oil emulsion	0.5
synthetic neutral hydrophilic silica (B.E.T. surface area: 200 m^2/g)	2.0
water q.s.p.	100

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Example 3

Following the procedure of Example 1, a concentrated oily suspension is prepared which has the following percentage composition by weight:

iprodione	37.5
mineral oil containing more than 70% of paraffins and having a hydrophilic/lipophilic balance with a value of 11 and dissolving 1 g of iprodione per litre of oil	20.0
ethylene glycol	5.0
condensates of 9—10 mols of ethylene oxide with synthetic C_{13} alcohols	1.0
acid phosphate of ethylene oxide/polystyryl phenol condensate	1.5
silicone oil emulsion	0.5
neutral hydrophilic precipitated silica (B.E.T. surface area: 300 m^2/g)	1.25
water q.s.p.	100

Example 4

Following the procedure of Example 1, a concentrated oily suspension is prepared which has the following percentage composition by weight:

iprodione	37.5
industrial groundnut oil solubilising 3.5 g of iprodione per litre	20.0
ethylene glycol	5.0
condensates of 9—10 mols of ethylene oxide with synthetic C_{13} alcohols	1.0
acid phosphate of ethylene oxide/polystyrylphenol condensate	2.0
silicone oil emulsion	0.5
neutral hydrophilic silica	1.0
water q.s.p.	100

Example 5

Following the procedure of Example 1, a concentrated oily suspension is prepared which has the following percentage composition by weight:

iprodione	26.0
paraffinic mineral oil (containing more than 70% of paraffin, having an HLB value of 10.5 and solubilising 4.5 g of iprodione per litre)	32.2
emulsifier based on condensates of 9—10 mols of ethylene oxide with synthetic C_{13} alcohols	0.8
phosphate of ethylene oxide/polystyrylphenol condensate	2.5
ethylene oxide/polyalkylphenol condensate	0.5
propylene glycol	5.0
heteropolysaccharide (Rhodopol 23)	0.65
formaldehyde (40% aqueous solution)	1.5
water q.s.p.	100

Example 6

Following the procedure of Example 1, a concentrated oily suspension is prepared which has the following percentage composition by weight and in which the iprodione is associated with another active ingredient, carbendazime, and the adjuvants are identical to those of Example 5:

iprodione	18.0
carbendazime	9.5
paraffinic mineral oil	28.0
emulsifier based on condensates of 9—10 mols of ethylene oxide with synthetic C_{13} alcohols	0.8
phosphate of ethylene oxide/polystyrylphenol condensate	2.5
ethylene oxide/polyalkylphenol condensate	0.5
propylene glycol	5.0
heteropolysaccharide (Rhodopol 23)	1.3
formaldehyde (40% aqueous solution)	3.0
water q.s.p.	100

The following tests illustrate the biological properties of iprodione compositions of the present invention.

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Open-air fungicide tests on *Botrytis cinerea* in vines

These tests were carried out on 50 m^2 vine plots by applying, for comparison purposes, an equal dose per hectare of a commercial wettable powder containing 50% by weight of iprodione, and of a composition according to Example 1, according to the following treatment programme:

First treatment

When the flower caps fall, in order to purify the dehydrated flower parts which can remain attached to the seeds and protect the stalk.

Second treatment

Before the bunch fills out, i.e. as long as it is still possible to reach the stalk by spraying, in order to protect it against a premature attack of rot.

Third treatment

When ripening starts, i.e. as from the time when the fruit becomes sensitive to attack by botrytis, which is responsible for grey rot in vines.

Fourth treatment

About three weeks before the vintage, in order to ensure that the harvest is in a healthy condition, at a period when the physiological and climatic conditions are frequently very favourable for the development of the fungus.

These treatments were carried out by pneumatic spraying at a low volume/hectare, i.e. from 100 to 300 litres/ha, directed towards the area of the bunches (localised applications) and at a dose per treatment of 750 g of active ingredient per hectare.

Contamination by botrytis took place naturally in the course of the months of September and October, which were damp with frequent night fogs.

Of course, some plots were left without treatment to act as controls.

When harvesting, the degree of rot in the fruit, compared with control plots of contaminated and untreated vines, was evaluated.

Under these conditions, it was observed that:

the plots of untreated control vines were attacked with an intensity of 41%, and

the commercial composition of iprodione as a 50% strength wettable powder has an average efficacy or protection of 34%, whereas the composition according to Example 1, applied at the same dose of active ingredient/hectare, effects a protection of 61%.

Furthermore, the composition according to Example 1 proved to be totally selective on vines.

Open-air fungicide tests on *Botrytis cinerea* in beans

These tests were carried out on 5 m^2 plots planted with beans, by applying, for comparison purposes, an equal dose per hectare of a commercial wettable powder containing 50% by weight of iprodione, and of a composition according to Example 1, according to the following programme, each treatment being carried out by pneumatic spraying at a low volume/ha (from 100 to 300 litres/ha), at a dose of 750 g/ha.

First treatment: when flowering starts.

Second treatment: when flowering ends.

Some plots were left without treatment to act as controls.

Contamination took place naturally.

Under these conditions, it was found when harvesting that:

the control plots were attacked to the extent of about 27%,

the plots treated with iprodione as a wettable powder were attacked to the extent of about 15%, and

the plots treated with iprodione formulated according to the invention were attacked to the extent of only 4.5%.

Test for rain resistance

15 cm high Eurocross B tomato plants were sprayed respectively with iprodione as a commercial wettable powder (50% by weight), and with iprodione formulated as in Example 1, the two formulations being applied at the same dose of 375 g of active ingredient per 1000 litres. The leaves were left to dry. A few plants were then subjected to different levels of artificial rainfall with the aid of a rain-simulating apparatus. Leaf samples were taken for each case of rainfall, inoculated with plugs of *Botrytis cinerea* mycelium and then left to incubate for 4 days at 20°C in an illuminated atmosphere saturated with moisture. Attack by the disease was then checked.

Under these conditions, it was observed that:

(a) as from watering with 5 mm of rainfall, the controls were completely contaminated,

(b) for 5 mm of rainfall, the samples treated with iprodione as a wettable powder were attacked

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to the extent of 56% in contrast to only 36% for those treated with iprodione formulated according to the invention, and

(c) for 10 mm of rainfall, the samples treated with iprodione as a wettable powder were attacked to the extent of 87% in contrast to only 31% for those treated with iprodione formulated according to the invention.

The test clearly show the significant and surprising improvement made to the efficacy of iprodione by using fluid compositions according to the invention.

Claims

1. An agricultural fluid fungicidal composition which contains, the percentages being by weight:

(a) from 20% to 40% of an active ingredient based on iprodione,

(b) an "oil-in-water" emulsion containing from 50% to 160%, relative to the iprodione, of an oil of which the hydrophilic/lipophilic balance (HLB) has a value of 8 to 12 on the scale of HLB values for the preparation of an "oil-in-water" emulsion,

(c) from 0.1% to 2% of a non-ionic emulsifier of the ethylene oxide/fatty alcohol condensate type, and

(d) optionally from 0.5% to 2.5% of a substantially neutral, hydrophilic silica.

2. A composition according to claim 1 in which the oil has a hydrophilic/lipophilic balance with a value of 10 to 11.

3. A composition according to claim 1 or 2 in which the oil can dissolve from 1 to 5 g of iprodione per litre at ambient temperature.

4. A composition according to claim 1, 2 or 3 in which the oil is a mineral oil.

5. A composition according to claim 1, 2 or 3 in which the oil is a vegetable oil.

6. A composition according to any one of claims 1 to 5 in which the oil has a viscosity between 20 and 30 cst.

7. A composition according to any one of claims 1 to 6 in which the non-ionic emulsifier is a condensate of one or more fatty alcohols containing from 12 to 14 carbon atoms with 8 to 12 mols of ethylene oxide.

8. A composition according to claim 7 in which the emulsifier is a condensate of synthetic alcohols containing 13 carbon atoms with 9—10 moles of ethylene oxide.

9. A composition according to any one of claims 1 to 8 in which the silica optionally present in the composition is a hydrated precipitated silica having a B.E.T. specific surface area of 200 to 300 m^2/g.

10. A composition according to any one of claims 1 to 9 in which solid particles of iprodione incorporated in the composition have an average diameter of less than 10 microns.

11. A composition according to any one of claims 1 to 9 in which solid particles of iprodione incorporated in the composition have an average diameter of 1 to 5 microns.

12. A composition according to any one of the preceding claims which includes as an adjuvant one or more of viscosity modifiers of the polysaccharide type, a dispersing-fluidising agent of the ethylene oxide/polyarylphenol condensate type, an anti-freeze agent, an anti-foam agent or a preservative for combatting microbial proliferations in the composition.

13. A composition according to claim 12 in which the viscosity modifier is a heteropolysaccharide resulting from the fermentation of carbohydrates by a microorganism of the xanthonomas type.

14. A composition according to any one of claims 1 to 13 in which carbendazime is, as an active ingredient, included in the composition.

15. A fungicidal composition according to claim 1 substantially as hereinbefore described in any one of Examples 1 to 6.

16. A method of protecting plants against fungal diseases which comprises applying to the plants of fluid fungicidal composition as claimed in any one of claims 1 to 15.

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