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54	FUNGICIDE MIXTURES

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57	Abstract (not more than 150 words) and figure of the drawings to which the abstract refers, are attached.	Number of sheets	28
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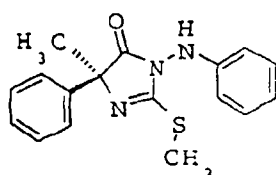
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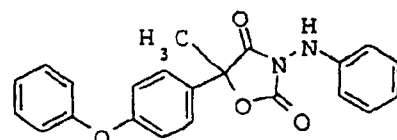
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(54) Title: FUNGICIDE MIXTURES

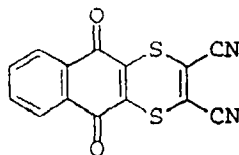
(54) Bezeichnung: FUNGIZIDE MISCHUNGEN



(Ia)



(Ib)



(II)

(57) Abstract: The invention relates to fungicide mixtures containing A) a phenylhydrazone (I) selected from the compounds of formulae (Ia) and (Ib), and B) a synergistically active quantity of the compound of formula (II). The invention also relates to a method for controlling pathogenic fungi using mixtures of compounds (I) and (II), and to the use of compounds (I) and (II) for producing said mixtures.

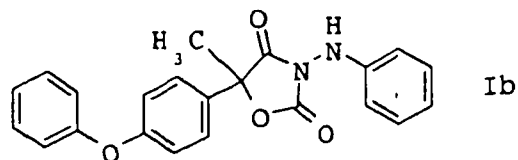
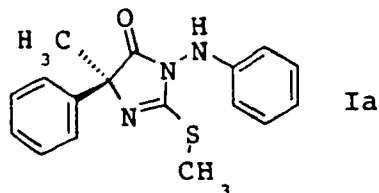
(57) Zusammenfassung: Fungizide Mischungen, enthaltend A) ein Phenylhydrazid I ausgewählt aus den Verbindungen (Ia) und (Ib) und B) die Verbindung der Formel (II) einer synergistisch wirksamen Menge, Verfahren zur Bekämpfung von Schadpilzen mit Mischungen der Verbindungen I und II und die Verwendung der Verbindungen I und II zur Herstellung derartiger Mischungen.

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Fungicidal mixtures

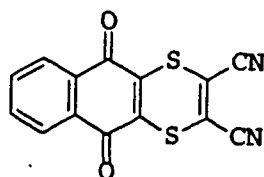
The present relates to fungicidal mixtures, comprising

A) a phenylhydrazide I selected from the compounds Ia and Ib



and

B) the compound of the formula II



in a synergistically effective amount.

Moreover, the invention relates to methods for controlling harmful fungi using mixtures of the compounds I and II, and to the use of the compounds I and II for preparing such mixtures, and compositions comprising them.

The compounds I, their preparation and their action against harmful fungi are known from the literature:

Compound No.	common name	Literature
Ia	fenamidone	Proc. Br. Crop. Prot. Conf, - Pests Dis. 1998, Vol. 1, p. 319
Ib	famoxadone	Proc. Br. Crop. Prot. Conf. - Pests Dis. 1996, Vol. 1, p. 21

The compound in the formula II (common name: dithianon) and processes for its preparation are described in GB-A 857 383.

However, the fungicidal activity of the known compounds and in particular the persistency of the phenylhydrazines I frequently leaves something to be desired.

Accordingly, a need exists to overcome the disadvantages mentioned and to provide fungicidal mixtures which have improved action, in particular persistency, against

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harmful fungi combined with a reduced total amount of active compounds applied (synergistic mixtures).

We have found that this need is fulfilled by the mixtures defined at the outset. Moreover, we have found that applying the compounds I and II simultaneously, either together or separately, or applying the compounds I and II in succession provides better control of harmful fungi than is possible with the individual compounds alone.

Usually, mixtures of the compound I with a phenylhydrazide II are used. However, in certain cases, mixtures of the compounds I and II with further fungicides may also be advantageous.

Particular preference is given to the compound Ia.

Owing to their basic character, the compounds Ia and Ib are capable of forming salts or adducts with inorganic or organic acids or with metal ions.

Examples of inorganic acids are hydrohalic acids, such as hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide, sulfuric acid, phosphoric acid, carbonic acid and nitric acid.

Suitable organic acids are, for example, formic acid, and alkanic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glycolic acid, thiocyanic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic acid, alkylsulfonic acid, (sulfonic acids having straight-chain or branched alkyl radicals with 1 to 20 carbon atoms), arylsulfonic acids or aryldisulfonic acids (aromatic radicals, such as phenyl and naphthyl, which carry one or two sulfo groups), alkylphosphonic acids (phosphonic acids having straight-chain or branched alkyl radicals with 1 to 20 carbon atoms), arylphosphonic acids or aryldiphosphonic acids (aromatic radicals, such as phenyl and naphthyl, which carry one or two phosphonic acid radicals), it being possible for the alkyl or aryl radicals to carry further substituents, for example p-toluenesulfonic acid, salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid, 2-acetoxybenzoic acid, etc.

Suitable metal ions are, in particular, the ions of the elements of the second main group, in particular calcium and magnesium, of the third and fourth main group, in particular aluminum, tin and lead, and of the first to eighth transition group, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc and

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others. Particular preference is given to the metal ions of the elements of the transition groups of the fourth period. The metals can be present in the various valencies which they can assume.

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When preparing the mixtures, it is preferred to employ the pure active compounds I and II, with which further active compounds against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active
10 compounds or fertilizers can be admixed as required.

The mixtures of the compounds I and II, or the simultaneous joint or separate use of the compounds I and II, have outstanding action against a wide range of phytopathogenic fungi, in
15 particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Phycomycetes* and *Basidiomycetes*.

They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable
20 species (for example cucumbers, beans and cucurbits), coffee, fruit species, soya, grapevine, ornamentals, and a variety of seeds.

They are particularly suitable for controlling the following
25 phytopathogenic fungi: *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* in cucurbits, *Podosphaera leucotricha* in apples, *Uncinula necator* in grapevines, *Venturia inaequalis* (scab) in apples, *Septoria nodorum* in wheat, *Botrytis cinerea* (gray mold) in strawberries, vegetables, ornamentals and grapevines,
30 *Cercospora arachidicola* in groundnuts, *Phytophthora infestans* in potatoes and tomatoes, *Pseudoperonospora* species in cucurbits and hops, *Plasmopara viticola* in grapevines, *Alternaria* species in vegetables and fruit and *Fusarium* and *Verticillium* species.

35 The compounds I and II can be applied simultaneously, either together or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the control results.

40 The compounds I and II are usually applied in a weight ratio of from 100:1 to 1:10, preferably from 10:1 to 1:1, in particular from 5:1 to 1:1.

Correspondingly, the application rates for the compound I are
45 generally from 5 to 2000 g/ha, preferably from 10 to 1000 g/ha, in particular from 50 to 750 g/ha.

Depending on the nature of the desired effect, the application rates of the mixtures according to the invention are, for the compounds II, from 5 g/ha to 500 g/ha, preferably from 50 to 500 g/ha, in particular from 50 to 200 g/ha.

5

For seed treatment, the application rates of the mixture are generally from 0.001 to 1 g/kg of seed, preferably from 0.01 to 0.5 g/kg, in particular from 0.01 to 0.1 g/kg.

- 10 If phytopathogenic harmful fungi are to be controlled, the separate or joint application of the compounds I and II or of the mixtures of the compounds I and II is effected by spraying or dusting the seeds, the plants or the soils before or after sowing, or before or after plant emergence.

15

The fungicidal synergistic mixtures according to the invention or the compounds I and II can be 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

- 20 suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, and applied by spraying, atomizing, dusting, broadcasting or watering. The use form depends on the intended purpose; in any case, it should ensure as fine and uniform a distribution as possible of the
- 25 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

30 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

- 35 dibutyl-naphthalenesulfonic acid, 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
- 40 naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl polyglycol ethers or tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide
- 45 condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether

5

acetate, sorbitol esters, lignosulfite waste liquors or methyl cellulose.

Powders, materials for broadcasting and dusts can be prepared by
5 mixing or jointly grinding the compounds I and II or the mixture of the compounds I and II with a solid carrier.

Granules (for example coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active
10 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,
15 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.

20 The formulations generally comprise from 0.1 to 95% by weight, preferably from 0.5 to 90% by weight, of one of the compounds I and II or of the mixture of the compounds I and II. The active compounds are employed in a purity of from 90% to 100%,
25 preferably from 95% to 100% (according to NMR or HPLC spectrum).

The compounds I and II, the mixtures or the corresponding formulations are applied by treating the harmful fungi, the plants, seeds, soils, areas, materials or spaces to be kept free
30 from them with a fungicidally effective amount of the mixture, or of the compounds I and II in the case of separate application. Application can be effected before or after infection by the harmful fungi.

35 Examples of such preparations comprising the active compounds are:

- I. a solution of 90 parts by weight of the active compounds and 10 parts by weight of N-methylpyrrolidone; this solution is
40 suitable for use in the form of microdrops;
- II. a mixture of 20 parts by weight of the active compounds, 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 mol of ethylene oxide to 1 mol of oleic acid
N-monoethanolamide, 5 parts by weight of the calcium salt of
45 dodecylbenzenesulfonic acid, 5 parts by weight of the adduct

- of 40 mol of ethylene oxide and 1 mol of castor oil; a dispersion is obtained by finely distributing the solution in water;
- III. an aqueous dispersion of 20 parts by weight of the active compounds, 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;
- IV. an aqueous dispersion of 20 parts by weight of the active compounds, 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction of boiling point 210 to 280°C, and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;
- V. a mixture, ground in a hammer mill, of 80 parts by weight of the active compounds, 3 parts by weight of the sodium salt of diisobutyl naphthalene-1-sulfonic acid, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel; a spray mixture is obtained by finely distributing the mixture in water;
- VI. an intimate mixture of 3 parts by weight of the active compounds and 97 parts by weight of finely divided kaolin; this dust comprises 3% by weight of active compound;
- VII. an intimate mixture of 30 parts by weight of the active compounds, 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel; this formulation imparts good adhesion to the active compound;
- VIII. a stable aqueous dispersion of 40 parts by weight of the active compounds, 10 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate, 2 parts by weight of silica gel and 48 parts by weight of water; this dispersion may be diluted further;
- IX. a stable oily dispersion of 20 parts by weight of the active compounds, 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 8 parts by weight of fatty alcohol polyglycol ether, 20 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate and 88 parts by weight of a paraffinic mineral oil.
- The fungicidal activity of the compound and of the mixtures can be demonstrated by the following experiments:
- The active compounds, separately or together, were formulated as a stock solution comprising 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on

ethoxylated alkylphenols) was added to the solution, and the mixture was diluted with water to the desired concentration.

Use example: Persistency against peronospora of grapevine caused by *Plasmopara viticola*

Leaves of potted grapevines of the cultivar "Müller-Thurgau" were sprayed to run off point with an aqueous suspension having the concentration of active compound stated below. To be able to assess the persistency of the substances, the plants were, after the spray coating had dried on, placed in a greenhouse for 3 days. Only then were the leaves inoculated with an aqueous zoospore suspension of *Plasmopara viticola*. The grapevines were then initially placed in a water-vapor-saturated chamber at 24°C for 48 hours and then in a greenhouse at temperatures between 20 and 30°C for 5 days. After this period of time, the plants were, to promote sporangiophore eruption, again placed in a humid chamber for 16 hours. The extent of the development of the infection on the undersides of the leaves was then determined visually.

for evaluation, the visually determined values for the percentages of infected leaf area were converted into efficacies in % of the untreated control.

25

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

30 α corresponds to the fungal infection of the treated plants in % and

β corresponds to the fungal infection of the untreated (control) plants in %

35

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

40 The expected efficacies of the active compound mixtures are determined using Colby's formula [R.S. Colby, Weeds 15, 20-22 (1967)] and compared with the observed efficacies.

Colby's formula:

45

$$E = x + y - x \cdot y / 100$$

E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b

5 x efficacy, expressed in % of the untreated control, when using active compound A at a concentration of a

y efficacy, expressed in % of the untreated control, when using active compound B at a concentration of b

10

Table A - Individual active compounds

	Example	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
15	1	Control (untreated)	(88% infection)	0
20	2	Ia (fenamidone)	6	94
			3	89
			1.5	93
			0.75	77
			0.375	66
25	3	Ib (famoxadone)	6	89
			3	89
			1.5	83
			0.75	77
			0.375	0
	4	II (dithianon)	15	32
			7.5	20
			3.75	0

30

Table B - Combinations according to the invention

	Example	Active compound mixture Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
35	5	Ia + II 1.5 + 15 ppm 1 : 10	100	88
	6	Ia + II 0.75 + 7.5 ppm 1 : 10	97	82
	7	Ia + II 0.375 + 3.75 ppm 1 : 10	100	66
40				
45	8	Ia + II 3 + 3.75 ppm 1 : 1.25	100	89

Example	Active compound mixture Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
9	Ia + II 6 + 3.75 ppm 1.6 : 1	100	94
10	Ib + II 1.5 + 15 ppm 1 : 10	100	88
11	Ib + II 0.75 + 7.5 ppm 1 : 10	94	82
12	Ib + II 0.375 + 3.75 ppm 1 : 10	77	0
13	Ib + II 3 + 3.75 ppm 1 : 1.25	100	89
14	Ib + II 6 + 3.75 ppm 1.6 : 1	100	89

*) efficacy calculated using Colby's formula

The test results show that, for all mixing ratios, the observed efficacy is higher than that predicted using Colby's formula.

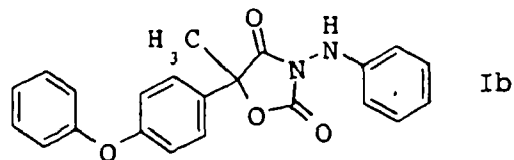
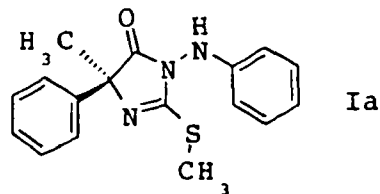
"Comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps or components or groups thereof.

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We claim:

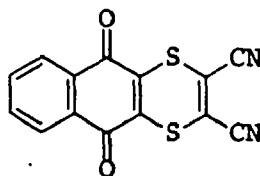
1. A fungicidal mixture, comprising

A) a phenylhydrazide I selected from the compounds Ia and Ib



and

B) the compound of the formula II



in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, comprising as phenylhydrazide II the compound IIa as set forth in claim 1.
3. A fungicidal mixture as claimed in claim 1 or 2, wherein the weight ratio of the compound I to the compound II is from 10:1 to 1:100.
4. A fungicidal composition comprising a solid or liquid carrier and a mixture as claimed in claim 1.
5. A method for controlling harmful fungi, which comprises treating the harmful fungi, their habitat, or the plants, seeds, soils, areas, materials or spaces or be kept free from them with a compound of the formula I and the compound of the formula II as set forth in claim 1.
6. A method as claimed in claim 5, which comprises treating the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them with from 5 to 2000 g/ha of the compound II as set forth in claim 1.
7. A method as claimed in claim 5, which comprises treating the harmful fungi, their habitat, or the plants, seeds soils, areas, materials or spaces to be kept free from

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them with from 5 to 500 g/ha of at least one compound I as set forth in claim 1.

8. The use of the compounds of the formulae I and II as set forth in claim 1 for preparing a mixture as claimed in claim 1.
9. A fungicidal mixture as claimed in any one of claims 1 to 3, substantially as hereinbefore described or exemplified.
10. A fungicidal mixture including any new and inventive integer or combination of integers, substantially as herein described.
11. A fungicidal composition as claimed in claim 4, substantially as hereinbefore described or exemplified.
12. A fungicidal composition including any new and inventive integer or combination of integers, substantially as herein described.
13. A method according to the invention for controlling harmful fungi, substantially as hereinbefore described or exemplified.
14. A method for controlling harmful fungi including any new and inventive integer or combination of integers, substantially as herein described.
15. A use of the compounds of the formulae I and II as claimed in claim 8, substantially as hereinbefore described or exemplified.
16. A use of the compounds of the formulae I and II including any new and inventive integer or combination of integers, substantially as herein described.

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Fungicidal mixtures

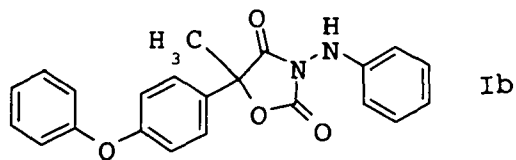
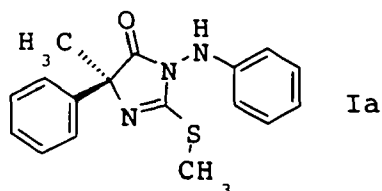
Abstract

5

Fungicidal mixtures, comprising

A) a phenylhydrazide I selected from the compounds Ia and Ib

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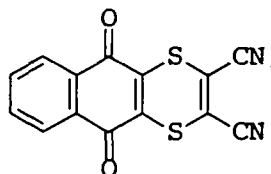


15

and

B) the compound of the formula II

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in a synergistically effective amount, methods for controlling harmful fungi using mixtures of the compounds I and II and the use of the compounds I and II for preparing such mixtures are described.

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