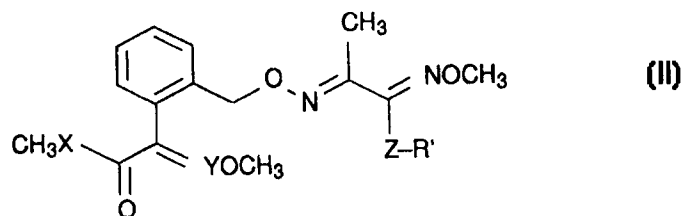
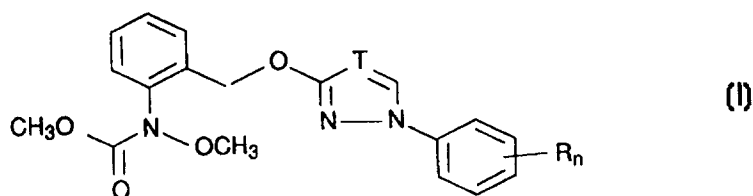




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(54) **MELANGES FUNGICIDES**
(54) **FUNGICIDE MIXTURES**



(57) L'invention concerne des mélanges fongicides contenant, en quantités à effet synergique, a) un carbamate de la formule (I) dans laquelle T désigne CH et N, n vaut 0, 1 ou 2 et R désigne halogène, alkyle

(57) This invention concerns a fungicide mixture containing, in synergistically effective quantities, a) a carbamate of the formula (I), in which T means CH or N, n stands for 0, 1 or 2 and R means halogen, C₁C₄-alkyl





C_1-C_4 ou halogénure d'alkyle C_1-C_4 , les restes R pouvant être différents lorsque n vaut 2, et/ou b) un éther d'oxime de la formule (II) dans laquelle les substituants ont la signification suivante: X désigne oxygène ou amino (NH); Y désigne CH ou N; Z désigne oxygène, soufre, amino (NH) ou alkylamino C_1-C_4 (N-alkyle C_1-C_4); R' désigne alkyle C_1-C_6 , halogénure d'alkyle C_1-C_6 , alcényle C_3-C_6 , halogénure d'alkyle C_2-C_6 , alcényle C_3-C_6 , halogénure d'alcényle C_3-C_6 , cycloalkyle C_3-C_6 -méthyle, ou benzyle, qui peut être halogéné partiellement ou entièrement et/ou peut porter entre un et trois des restes suivants: cyano, alkyle C_1-C_4 , halogénure d'alkyle C_1-C_4 , alcoxy C_1-C_4 , halogénure d'alcoxy C_1-C_4 et alkylthio C_1-C_4 ; c) un carbamate de la formule (III)
 $(CH_3)_2N-CH_2CH_2CH_2-NH-CO_2-CH_2CH_2CH_3$.

or C_1C_4 -alkyl halide, where the radicals R can be different, if n stands for 2 and/or b) an oxime ether of the formula (II), in which the substituents have the following meaning: X is oxygen or amino (NH); Y is CH or N; Z is oxygen, sulphur, amino (NH) or C_1C_4 -alkyl amino (N- C_1C_4 -alkyl); R' is C_1C_6 -alkyl, C_1C_6 -alkyl halide, C_3-C_6 -alkenyl, C_2C_6 -alkenyl halide, C_3-C_6 -alkenyl, C_3-C_6 -alkinyl halide, C_3-C_6 -cycloalkyl-methyl, or benzyl, which can be either partially or completely halogenized and/or can carry one to three of the following radicals: cyano, C_1C_4 -alkyl, C_1C_4 -alkyl halide, C_1C_4 -alkoxy, C_1C_4 -alkoxy halide, and C_1C_4 -alkylthio; c) a carbamate of the formula (III)
 $(CH_3)_2N-CH_2CH_2CH_2-NH-CO_2-CH_2CH_2CH_3$ (III).



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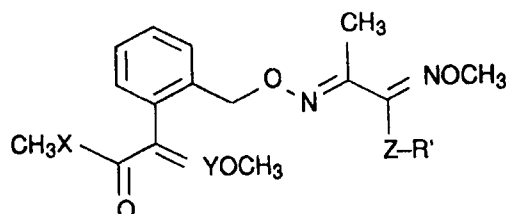
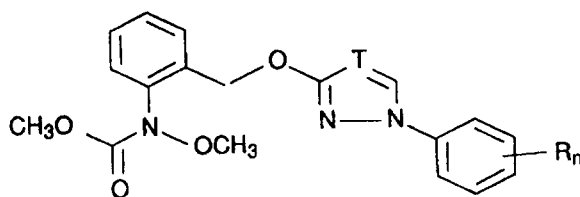
(51) Internationale Patentklassifikation ⁶: A01N 37/52, 47/24 // (A01N 37/52, 47:12) (A01N 47/24, 47:12)	A1	(11) Internationale Veröffentlichungsnummer: WO 97/40678 (43) Internationales Veröffentlichungsdatum: 6. November 1997 (06.11.97)
(21) Internationales Aktenzeichen: PCT/EP97/02048 (22) Internationales Anmeldedatum: 23. April 1997 (23.04.97) (30) Prioritätsdaten: 196 16 689.6 26. April 1996 (26.04.96) DE 196 17 069.9 29. April 1996 (29.04.96) DE 196 35 505.2 2. September 1996 (02.09.96) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AKTIENGESellschaft [DE/DE]; D-67056 Ludwigshafen (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): MÜLLER, Bernd [DE/DE]; Jean-Ganss-Strasse 21, D-67227 Frankenthal (DE). SAUTER, Hubert [DE/DE]; Neckarpromenade 20, D-68167 Mannheim (DE). AMMERMAN, Eberhard [DE/DE]; Von-Gagern-Strasse 2, D-64646 Heppenheim (DE). LORENZ, Gisela [DE/DE]; Erlenweg 13, D-67434 Hambach (DE). STRATHMANN, Siegfried [DE/DE]; Donnersbergstrasse 9, D-67117 Limburgerhof (DE). SCHELBERGER, Klaus [DE/DE]; Traminerweg 2, D-67161 Gönheim (DE). SCHERER, Maria [DE/DE]; Hermann-Jürgens-Strasse 30, D-76829 Landau (DE). MAPPE, Dietrich [DE/DE]; Wiesenweg 145, D-67368	Westheim (DE). LEYENDECKER, Joachim [DE/DE]; Stahlbühlring 79, D-68526 Ladenburg (DE). BAYER, Herbert [DE/DE]; D 3.4, D-68159 Mannheim (DE). MÜLLER, Ruth [DE/DE]; Von-Wieser-Strasse 1, D-67159 Friedelsheim (DE). (74) Gemeinsamer Vertreter: BASF AKTIENGESellschaft; D-67056 Ludwigshafen (DE). (81) Bestimmungsstaaten: AU, BG, BR, CA, CN, CZ, GE, HU, IL, JP, KR, LV, MX, NO, NZ, PL, RO, SG, SI, SK, TR, UA, US, eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Veröffentlicht Mit internationalem Recherchenbericht.	

(54) Title: FUNGICIDE MIXTURES

(54) Bezeichnung: FUNGIZIDE MISCHUNGEN

(57) Abstract

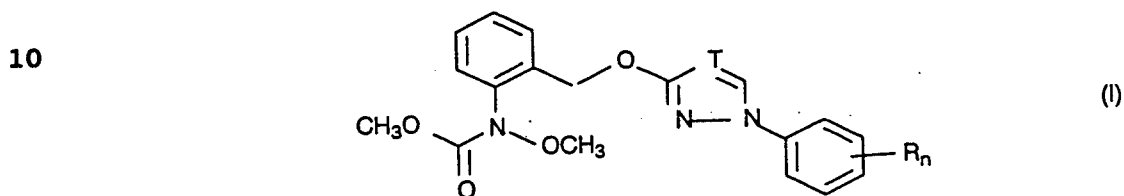
This invention concerns a fungicide mixture containing, in synergistically effective quantities, a) a carbamate of the formula (I), in which T means CH or N, n stands for 0, 1 or 2 and R means halogen, C₁C₄-alkyl or C₁C₄-alkyl halide, where the radicals R can be different, if n stands for 2 and/or b) an oxime ether of the formula (II), in which the substituents have the following meaning: X is oxygen or amino (NH); Y is CH or N; Z is oxygen, sulphur, amino (NH) or C₁C₄-alkyl amino (N-C₁C₄-alkyl); R' is C₁C₆-alkyl, C₁C₆-alkyl halide, C₃-C₆-alkenyl, C₂C₆-alkenyl halide, C₃-C₆-alkenyl, C₃-C₆-alkinyl halide, C₃-C₆-cycloalkyl-methyl, or benzyl, which can be either partially or completely halogenized and/or can carry one to three of the following radicals: cyano, C₁C₄-alkyl, C₁C₄-alkyl halide, C₁C₄-alkoxy, C₁C₄-alkoxy halide, and C₁C₄-alkylthio; c) a carbamate of the formula (III) (CH₃)₂N-CH₂CH₂CH₂-NH-CO₂-CH₂CH₂CH₃ (III).



Fungicide mixtures

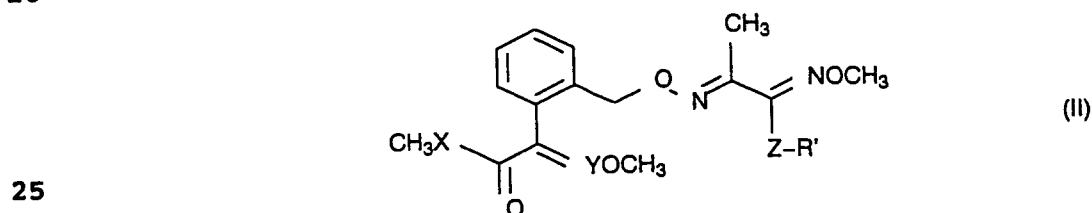
The present invention relates to a fungicidal mixture which
5 comprises

a) a carbamate of the formula I



15 where T is CH or N, n is 0, 1 or 2 and R is halogen, C₁-C₄-alkyl or C₁-C₄-haloalkyl, it being possible for the radicals R to be different when n is 2, and/or

20 b) an oxime ether of the formula II,



where the substituents have the following meanings:

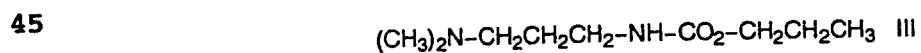
30 X is oxygen or amino (NH);

Y is CH or N;

35 Z is oxygen, sulfur, amino (NH) or C₁-C₄-alkylamino (N-C₁-C₄-alkyl);

40 R' is C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₃-C₆-alkenyl, C₂-C₆-haloalkenyl, C₃-C₆-alkynyl, C₃-C₆-haloalkynyl, C₃-C₆-cycloalkylmethyl, or is benzyl which can be partially or fully halogenated and/or can have attached to it one to three of the following radicals: cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and C₁-C₄-alkylthio;

c) a carbamate of the formula III



2

in a synergistically active amount.

Moreover, the invention relates to methods of controlling harmful fungi with mixtures of the compounds I and/or II and III and to
5 the use of the compounds I and/or II and the compound III for the preparation of such mixtures.

The compounds of the formula I, their preparation and their action against harmful fungi has [sic] been disclosed in the
10 literature (WO-A 96/01,256 and WO-A 96/01,258).

Compounds of the formula II, their preparation and their action against harmful fungi have been described in WO-A 95/21,153, WO-A 95/21,154 and DE 1 95 28 651.0.

15

The compound III (German Laid-Open Application DOS 15 67 169, common name: propamocarb), its preparation and its action against harmful fungi have also been disclosed.

20 It was an object of the present inventions [sic] to provide mixtures which have an improved activity gainst harmful fungi combined with a reduced total amount of active ingredients applied (synergistic mixtures) with a view to reducing the rates of application and to improving the spectrum of action of the
25 known compounds.

Accordingly, we have found that this object is achieved by the mixture defined at the outset. Moreover, we have found that better control of the harmful fungi is possible by applying the
30 compounds I and/or II and the compound III simultaneously together or separately or by applying the compounds I and/or II and the compound III in succession than when the individual compounds are used.

35 In particular, the formula I represents carbamates in which the combination of the substituents corresponds to one line of the table which follows:

	No.	T	R _n
40	I.1	N	2-F
	I.2	N	3-F
	I.3	N	4-F
	I.4	N	2-Cl
	I.5	N	3-Cl
45	I.6	N	4-Cl
	I.7	N	2-Br

3

	No.	T	R _n
5	I.8	N	3-Br
	I.9	N	4-Br
	I.10	N	2-CH ₃
	I.11	N	3-CH ₃
	I.12	N	4-CH ₃
10	I.13	N	2-CH ₂ CH ₃
	I.14	N	3-CH ₂ CH ₃
	I.15	N	4-CH ₂ CH ₃
	I.16	N	2-CH(CH ₃) ₂
	I.17	N	3-CH(CH ₃) ₂
15	I.18	N	4-CH(CH ₃) ₂
	I.19	N	2-CF ₃
	I.20	N	3-CF ₃
	I.21	N	4-CF ₃
	I.22	N	2,4-F ₂
20	I.23	N	2,4-Cl ₂
	I.24	N	3,4-Cl ₂
	I.25	N	2-Cl, 4-CH ₃
	I.26	N	3-Cl, 4-CH ₃
	I.27	CH	2-F
25	I.28	CH	3-F
	I.29	CH	4-F
	I.30	CH	2-Cl
	I.31	CH	3-Cl
	I.32	CH	4-Cl
30	I.33	CH	2-Br
	I.34	CH	3-Br
	I.35	CH	4-Br
	I.36	CH	2-CH ₃
	I.37	CH	3-CH ₃
35	I.38	CH	4-CH ₃
	I.39	CH	2-CH ₂ CH ₃
	I.40	CH	3-CH ₂ CH ₃
	I.41	CH	4-CH ₂ CH ₃
	I.42	CH	2-CH(CH ₃) ₂
40	I.43	CH	3-CH(CH ₃) ₂
	I.44	CH	4-CH(CH ₃) ₂
	I.45	CH	2-CF ₃
	I.46	CH	3-CF ₃

4

No.	T	R _n
I.47	CH	4-CF ₃
I.48	CH	2,4-F ₂
I.49	CH	2,4-Cl ₂
I.50	CH	3,4-Cl ₂
I.51	CH	2-Cl, 4-CH ₃
I.52	CH	3-Cl, 4-CH ₃

¹⁰ The compounds I.12, I.23, I.32 and I.38 are especially preferred.

In particular, the general formula II represents methoxyacrylates and oxime ethers where X is oxygen and Y is CH, or X is amino and Y is N.

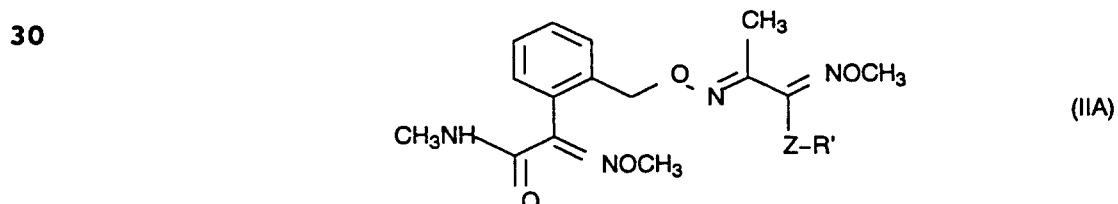
Moreover, preferred compounds II are those where Z is oxygen.

Equally, preferred compounds II are those where R' is alkyl or benzyl.

Particularly preferred with a view to their use in the synergistic mixtures according to the invention are the compounds II which are compiled in the tables below:

25 Table 2.

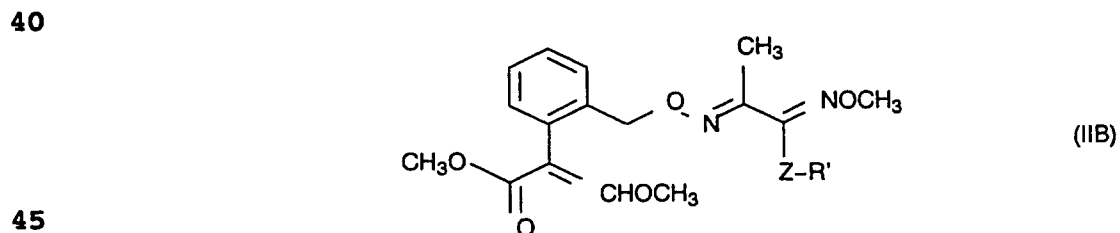
Compounds of the formula IIA where ZR' for each compound corresponds to one line of Table A.



35

Table 3.

Compounds of the formula IIB where ZR' for each compound corresponds to one line of Table A



45

Table A:

No.	ZR'
5	II.1 O-CH ₂ CH ₂ CH ₃
	II.2 O-CH(CH ₃) ₂
	II.3 O-CH ₂ CH ₂ CH ₂ CH ₃
	II.4 O-CH(CH ₃)CH ₂ CH ₃
	II.5 O-CH ₂ CH(CH ₃) ₂
10	II.6 O-C(CH ₃) ₃
	II.7 S-C(CH ₃) ₃
	II.8 O-CH(CH ₃)CH ₂ CH ₂ CH ₃
	II.9 O-CH ₂ C(CH ₃) ₃
15	II.10 O-CH ₂ C(Cl)=CCl ₂
	II.11 O-CH ₂ CH=CH-Cl (trans)
	II.12 O-CH ₂ C(CH ₃)=CH ₂
	II.13 O-CH ₂ -(cyclopropyl)
20	II.14 O-CH ₂ -C ₆ H ₅
	II.15 O-CH ₂ -[4-F-C ₆ H ₄]
	II.16 O-CH ₂ CH ₃
	II.17 O-CH(CH ₂ CH ₃) ₂

25 Relative to the C=Y double bond, the compounds of the formula II can exist in the E or the Z configuration (relative to the carboxylic acid function). Accordingly, they can be used in the mixture according to the invention in each case either in the form of pure E or Z isomers or as an E/Z isomer mixture. Preferred in
30 each case is the E/Z isomer mixture or the E isomer, the E isomer being especially preferred in the case of the compound II.

The C=N double bonds of the oxime ether groups in the side chain of the compounds II can exist in each case in the form of pure E or Z isomers or as E/Z isomer mixtures. The compounds II can be
35 used as isomer mixtures and also as pure isomers in the mixtures according to the invention. With a view to their use, compounds II which are particularly preferred are those where the terminal oxime ether group in the side chain is in the cis configuration
40 (OCH₃ group relative to ZR').

Due to the basic character, the compounds I and II are capable of forming adducts or salts with inorganic or organic acids or with metal ions.

6

Examples of inorganic acids are hydrohalic acids such as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid, sulfuric acid, phosphoric acid and nitric acid.

- 5 Suitable organic acids are, for example, formic acid, carbonic acid [sic] and alkanolic 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,
- 10 alkylsulfonic acids (sulfonic acids having straight-chain or branched alkyl radicals having from 1 to 20 carbon atoms), arylsulfonic acids or -disulfonic acids (aromatic radicals such as phenyl and naphthyl which have attached to them one or two sulfo groups), alkylphosphonic acids (phosphonic acids having
- 15 straight-chain or branched alkyl radicals of from 1 to 20 carbon atoms), arylphosphonic acids or -diphosphonic acids (aromatic radicals such as phenyl and naphthyl which have attached to them one or two phosphoric [sic] acid radicals), it being possible for the alkyl or aryl radicals to have attached to them further
- 20 substituents, eg. 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
- 25 of the second main group, in particular calcium and magnesium, and of the third and fourth main group, in particular aluminum, tin and lead, and of the first to eighth sub-group, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc and others. Especially preferred are the metal ions of the elements
- 30 of the sub-groups of the fourth period. The metals can in this case be in the various valences which they can assume.

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

- The mixtures of the compounds I and/or II and III, or the
- 40 simultaneous joint or separate use of the compounds I and/or II and III, are distinguished by an outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Deuteromycetes, Phycomycetes and Basidiomycetes. Some of them act systemically and can therefore
- 45 be employed as foliar- and soil-acting fungicides.

7

They are especially important for controlling a large number of fungi in a variety of crop plants such as cotton, vegetable species (eg. cucumbers, beans and curcubits), barley, grass, oats, coffee, corn, fruit species, rice, rye, soybeans, 5 grapevine, wheat, ornamentals, sugar cane, and a variety of seeds.

They are particularly suitable for controlling the following phytopathogenic fungi: *Erysiphe graminis* (powdery mildew) on 10 cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* on curcubits, *Podosphaera leucotricha* on apples, *Puccinia* species on cereals, *Rhizoctonia* species on cotton, rice and lawn, *Ustilago* species on cereals and sugar cane, *Venturia inaequalis* (scab) on apples, *Helminthosporium* species on cereals, *Septoria nodorum* on 15 wheat, *Botrytis cinera* [sic] (gray mold) on strawberries, vegetables, ornamentals and grapevines, *Cercospora arachidicola* on peanuts, *Pseudocercospora herpotrichoides* on wheat and barley, *Pyricularia oryzae* on rice, *Phytophthora infestans* on potatoes and tomatoes, *Pseudoperonospora* species on cucurbits and 20 hops, *Plasmopara viticola* on grapevines, *Alternaria* species on vegetables and fruit, and *Fusarium* and *Verticillium* species.

Furthermore, they can be used in the protection of materials (eg. in the protection of wood), for example against *Paecilomyces* 25 *variotii*.

The compounds I and/or II and III can be applied simultaneously together or separately or in succession, the sequence, in the case of separate application, generally not having any effect on 30 the result of the control measures.

The compounds I and/or II and III are normally used in a weight ratio of from 200:1 to 0.1:1, preferably 100:1 to 1:1, in particular 50:1 to 5:1 (III:I and/or II).

35

The application rates of the mixtures according to the invention are, in the case of the compounds I and/or II, in general from 0.005 to 0.5 kg/ha, preferably 0.01 to 0.5 kg/ha, in particular 0.01 to 0.3 kg/ha, depending on the nature of the desired effect.

40

Correspondingly, in the case of the compound III, the application rates are from 0.1 to 10 kg/ha, preferably 0.5 to 5 kg/ha, in particular 1 to 4 kg/ha.

45

8

For seed treatment, the application rates of the mixture are generally from 0.001 to 100 g/kg seed, preferably 0.01 to 50 g/kg, in particular 0.01 to 10 g/kg.

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

- The fungicidal synergistic mixtures according to the invention, or the compounds I and/or II and III, can be formulated for example in the form of ready-to-spray solutions, powders and
15 suspensions or in the form of highly concentrated aqueous, oily or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading or granules, and applied by spraying, atomizing, dusting, spreading or pouring. The use form depends on the intended purpose; in any case, it should
20 guarantee as fine and uniform as possible a distribution of the mixture according to the invention.

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

- Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, eg.
30 ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, of alkyl- and alkylarylsulfonates, of alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols or fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives
35 with formaldehyde, condensates of naphthalene, or of the naphthalenesulfonic acids, with phenol and formaldehyde, polyoxyethylene octylphenol [sic] ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenol [sic] polyglycol ethers or tributylphenyl polyglycol ether, alkylaryl polyether alcohols,
40 isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene [sic], lauryl alcohol polyglycol ether acetate, sorbitol esters, lignin-sulfite waste liquors or methylcellulose.

9

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

5

Granules (eg. coated granules, impregnated granules or homogeneous granules) are normally prepared by binding the active ingredient, or active ingredients, to a solid carrier.

- 10 Fillers or solid carriers are, for example, mineral earths such as silica gel, silicas, silica gels [sic], silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, and fertilizers such as
- 15 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 0.5 to 90% by weight, of one of the compounds I and/or II or III, or of the mixture of the compounds I and/or II and III. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR or HPLC
- 25 spectrum [sic]).

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

- 35 The fungicidal activity of the compounds and of the mixtures is demonstrated by the following experiments:

- The active ingredients, separately or together, are formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone,
- 40 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) and 10% by weight of Emulphor® EL (Emulan® EL, emulsifier based on ethoxylated fatty alcohols) and diluted with water to give the desired concentration.

45

10

Evaluation is carried out by determining the infected leaf areas in percent. These percentages are converted into efficacies. The expected efficacies of the mixtures of the active ingredients are determined using Colby's formula [R.S. Colby, Weeds 15, 20-22 5 (1967)] and compared with the observed efficacies.

Colby's formula:

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

10

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

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

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

20

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

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

25 α is the fungal infection of the treated plants in % and

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

30 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 are not infected.

Examples 1-10

35 Efficacy against *Phytophthora infestans* on tomatoes

Leaves of potted plants cv. "Große Fleischtomate" were sprayed to run-off with an aqueous suspension made with a stock solution of 10% active ingredient, 63% cyclohexanone and 27% emulsifier. The 40 next day, the leaves were inoculated with an aqueous zoospore suspension of *Phytophthora infestans*. The plants were subsequently placed into a water-vapor-saturated chamber at from 16 to 18°C. After 6 days, the blight had developed to such an extent on the untreated, but inoculated, control plants that it was pos- 45 sible to determine the disease level visually in %.

11

The visually determined values for the percentage of diseased leaf area were transformed into efficacies as % of the untreated control. An efficacy of 0 is the same disease level as in the untreated control, an efficacy of 100 is a disease level of 0%. The expected efficacies for combinations of active ingredients were determined using Colby's formula (Colby, S.R. (Calculating synergistic and antagonistic responses of herbicide Combinations", Weeds, 15, p. 20-22, 1967) and compared with the observed efficacies.

10

Table 4

15	Ex.	Active ingredient	Concentration of active ingredient in the spray mixture in ppm	Efficacy in % of the untreated control
	1v	Control (untreated)	(disease level 98%)	0
	2v	A = Tab. 2A, No. II.2	16 4 1	8 8 0
20	3v	B = Tab. 2A, No. II.4	16 4 1	39 0 0
25	4v	III = propamocarb	125 63 31 16	18 8 8 0

Table 5

30	Ex.	Concentration of active ingredient in the spray mixture in ppm	Observed efficacy	Calculated efficacy *)
	5	16A + 16III	49	8
35	6	16A + 31III	49	15
	7	16A + 63III	39	15
40	8	16A + 125III	69	24

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9	16B + 31III	59	43
10	16B + 63III	59	43

*) calculated using Colby's formula

The results of Example [sic] 1-10 demonstrate that the observed 10 efficacy in all mixing ratios exceeds the efficacy precalculated using Colby's formula.

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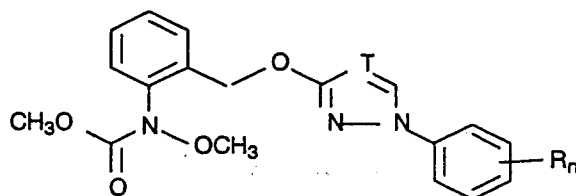
We claim:

1. A fungicidal mixture comprising

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a) a carbamate of the formula I

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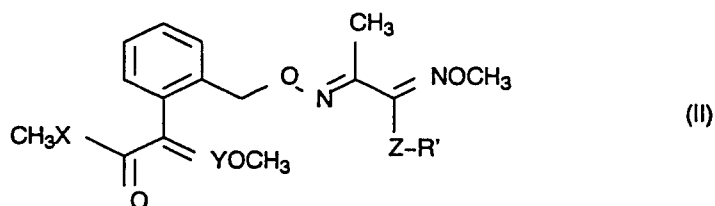


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where T is CH or N, n is 0, 1 or 2 and R is halogen, C₁-C₄-alkyl or C₁-C₄-haloalkyl, it being possible for the radicals R to be different when n is 2, and/or

b) an oxime ether of the formula II,

20



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where the substituents have the following meanings:

30

X is oxygen or amino (NH);

Y is CH or N;

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Z is oxygen, sulfur, amino (NH) or C₁-C₄-alkylamino (N-C₁-C₄-alkyl);

40

R' is C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₃-C₆-alkenyl, C₂-C₆-haloalkenyl, C₃-C₆-alkynyl, C₃-C₆-haloalkynyl, C₃-C₆-cycloalkylmethyl, or is benzyl which can be partially or fully halogenated and/or can have attached to it one to three of the following radicals: cyano, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and C₁-C₄-alkylthio;

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c) a carbamate of the formula III



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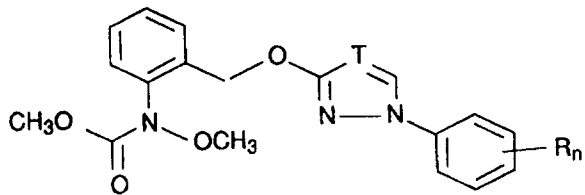
in a synergistically active amount.

2. A fungicidal mixture as claimed in claim 1 wherein the weight ratio of the compound III to the compound I and/or II is
5 200:1 to 0.1:1.
3. A method of controlling harmful fungi, which comprises treating the harmful fungi, their environment, or the plants, seeds, soils, areas, materials or spaces to be kept free from
10 them with a compound of the formula I and/or a compound of the formula II as set forth in claim 1 and the compound of the formula III as set forth in claim 1 in a synergistically active amount.
- 15 4. A method as claimed in claim 3, wherein a compound I and/or a compound of the formula II as set forth in claim 1 and the compound III as set forth in claim 1 are applied simultaneously together or separately or in succession.
- 20 5. A method as claimed in claim 3, wherein the harmful fungi, their environment, or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with from 0.005 to 0.5 kg/ha of a compound I and/or a compound of the formula II as set forth in claim 1.
- 25 6. A method as claimed in claim 3, wherein the harmful fungi, their environment, or the plants, seeds, soils, areas, materials or spaces to be kept free from them are treated with from 0.1 to 10 kg/ha of the compound III as set forth in
30 claim 1.

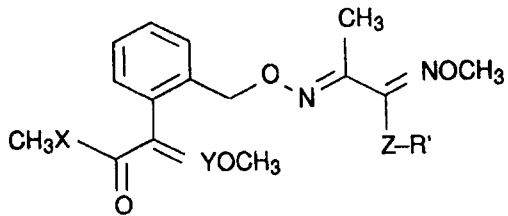
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(I)



(II)