

**(19) AUSTRALIAN PATENT OFFICE**

(54) Title  
Dithianon-based fungicidal mixtures

(51)<sup>6</sup> International Patent Classification(s)  
**A01N** 43/32 (2006.01) <sup>8BMEP</sup> **A01N**  
**A01N** 43/54 (2006.01) 43/54  
A01N 43/32 20060101ALI2005100  
20060101AFI2005100 <sup>8BMEP</sup>  
PCT/EP2003/006887

(21) Application No: 2003246634 (22) Application Date: 2003 .06 .30

(87) WIPO No: W004/004461

(30) Priority Data

(31) Number	(32) Date	(33) Country
102 30 802.0	2002 .07 .08	DE

(43) Publication Date : 2004 .01 .23

(43) Publication Journal Date : 2004 .03 .11

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(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum  
Internationales Büro



(43) Internationales Veröffentlichungsdatum  
15. Januar 2004 (15.01.2004)

PCT

(10) Internationale Veröffentlichungsnummer  
WO 2004/004461 A1

- (51) Internationale Patentklassifikation: A01N 43/32, 43/54 // (A01N 43/32, 43:54) Randall, Even [US/DE]; Birkenweg 3, 67283 Obrißheim (DE).
- (21) Internationales Aktenzeichen: PCT/EP2003/006887 (74) Gemeinsamer Vertreter: BASF AKTIENGESELLSCHAFT; 67056 Ludwigshafen (DE).
- (22) Internationales Anmeldedatum: 30. Juni 2003 (30.06.2003) (81) Bestimmungsstaaten (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (25) Einreichungssprache: Deutsch
- (26) Veröffentlichungssprache: Deutsch
- (30) Angaben zur Priorität: 102 30 802.0 8. Juli 2002 (08.07.2002) DE (84) Bestimmungsstaaten (regional): ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
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Veröffentlicht:

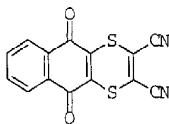
— mit internationalem Recherchenbericht

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

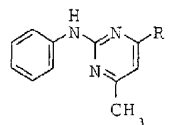
(54) Title: DITHIANON-BASED FUNGICIDAL MIXTURES

(54) Bezeichnung: FUNGIZIDE MISCHUNGEN AUF BASIS VON DITHIANON

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(I)



(II)

(57) Abstract: The invention relates to fungicidal mixtures that contain A) the compound of formula (I), and B) a pyrimidine derivative of formula (II), wherein R represents methyl, cyclopropyl or 1-propinyl, in a synergistically effective amount. The invention also relates to a method for controlling parasitic fungi using mixtures of the compounds (I) and (II) and the use of compounds (I) and (II) in the production of such mixtures.


(57) Zusammenfassung: Fungizide Mischungen, enthaltend A) die Verbindung der Formel (I) und B) ein Pyrimidinderivat der Formel (II), in der R für Methyl, Cyclopropyl oder 1-Propinyl steht, in 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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IN THE MATTER OF an Australian  
Application corresponding to  
PCT Application PCT/EP03/06887

RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England, hereby solemnly and sincerely declares that, to the best of its knowledge and belief, the following document, prepared by one of its translators competent in the art and conversant with the English and German languages, is a true and correct translation of the PCT Application filed under No. PCT/EP03/06887.

Date: 18 October 2004



S. ANTHONY

Director

For and on behalf of RWS Group Ltd

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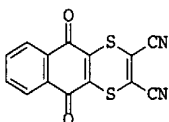
Fungicidal mixtures based on dithianon

The present invention relates to fungicidal mixtures, comprising

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A) the compound of the formula I

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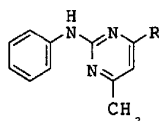


I

and

B) a pyrimidine derivative of the formula II,

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II

20 in which R is methyl, cyclopropyl or 1-propynyl 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.

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

30 The compounds of the formula II, their preparation and their action against harmful fungi are likewise known from the literature:

Compound No.	R	common name	Literature
35 II-1	methyl	pyrimethanil	DD-A 151 404
II-2	cyclopropyl	cyprodinil	EP-A 310 550
II-3	1-propynyl	mepanipyrim	EP-A 224 339

It is an object of the present invention to provide mixtures which have improved activity against harmful fungi combined with a reduced total amount of active compounds applied (synergistic mixtures), with a view to reducing the application rates of broadening the activity spectrum of the known compounds.

We have found that this object is achieved by the mixtures defined at the outset. Moreover, we have found that applying the compounds I and II simultaneously, i.e. together or separately, or applying the compounds I and II in succession provides better

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control of harmful fungi than is possible with the individual compounds alone.

Usually, what are applied are mixtures of the compound I with one  
5 pyrimidine derivative II. However, in certain cases mixtures of  
the compound I with two or more pyrimidine derivatives II may be  
advantageous.

Particular preference is given to the compounds II-1 and II-2.

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Owing to their basic character, the compounds II-1 to II-3 are  
capable of forming salts or adducts with inorganic or organic  
acids or with metal ions.

15 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.

20 Suitable organic acids are, for example, formic acid, and  
alkanoic 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 acids (sulfonic  
25 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  
30 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,  
35 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  
40 lead, and of the first to eighth transition group, in particular  
chromium, manganese, iron, cobalt, nickel, copper, zinc, and  
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 valences which they can  
45 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 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 particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Oomycetes* and *Basidiomycetes*. Some of them act systemically and are therefore also suitable for use as foliar- and soil-acting fungicides.

They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable species (for example cucumbers, beans and cucurbits), barley, grass, oats, coffee, corn, fruit species, rice, rye, soya, grapevine, wheat, ornamentals, sugarcane, and a variety of seeds.

They are particularly suitable for controlling the following phytopathogenic fungi: *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* in cucurbits, *Podosphaera leucotricha* in apples, *Uncinula necator* in grapevines, *Rhizoctonia* species in cotton, rice and lawns, *Ustilago* species in cereals and sugarcane, *Venturia inaequalis* (scab) in apples, *Septoria nodorum* in wheat, *Botrytis cinerea* (gray mold) in strawberries, vegetables, ornamentals and grapevines, *Cercospora arachidicola* in groundnuts, *Pseudocercospora herpotrichoides* in wheat and barley, *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.

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

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

Correspondingly, the application rates of the compound I are generally from 5 to 2 000 g/ha, preferably from 10 to 1 000 g/ha, in particular from 50 to 750 g/ha.

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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.

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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.

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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 each case, it should ensure as fine and uniform a distribution as possible of the mixture according to the invention.

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

Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, for example ligno-, phenol-, naphthalene- and

35 dibutyl-naphthalenesulfonic acids, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, or of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of

40 naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates,

45 ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether

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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 spectrum or HPLC).

The compounds I and II, the mixtures or the corresponding  
formulations are applied by treating the harmful fungi, or 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  
40 solution is 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  
45 of dodecylbenzenesulfonate, 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;
- 5 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;
- 10 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-sulfonate, 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;
- 15 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;
- 20 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;
- 25 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;
- 30 IX. a stable oily dispersion of 20 parts by weight of the active compounds, 2 parts by weight of the calcium salt of dodecylbenzenesulfonate, 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.
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The fungicidal activity of the compound and of the mixtures can be demonstrated by the following experiments:

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The active compounds, separately or together, were prepared as a stock solution with 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 this solution, and the solution was diluted with water to the desired concentration.

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Use example: Activity against early blight of tomato caused by *Alternaria solani*

Leaves of potted plants of the cultivar "Große Fleischtomate St. Pierre" were sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. The next day, the leaves were infected with an aqueous spore suspension of *Alternaria solani* in a 2% strength biomalt solution having a density of  $0.17 \times 10^6$  spores/ml. The plants were then placed in a water-vapor-saturated chamber at 20-22°C. After 5 days, the early blight on the untreated, but infected control plants had developed to such an extent that the infection could be determined visually in %.

Evaluation is carried out by determining the infected leaf areas in percent. These percentages are converted into efficacies.

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

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

$\alpha$  corresponds to the fungal infection of the treated plants in % and

$\beta$  corresponds to the fungal infection of the untreated (control) plants in %

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.

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

Colby's Formula:

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

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

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

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

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Table A - individual active compounds

Example	Active compound	Concentration of active compound in the spray liquid [ppm]	Efficacy in % of the untreated control	
5	1	Control (untreated)	(72% infection) 0	
10	2	I (dithianon)	63	86
			31	79
			16	65
			8	44
15	3	II-1 (pyrimethanil)	63	0
			31	0
			16	0
			8	0
20	4	II-2 (cyprodinil)	63	86
			16	72
			8	44

20 Table B - combinations according to the invention

Example	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)					
25	6	I + II-1 63 + 8 ppm 8 : 1	99	85				
30	7	I + IIa 15 + 1.5 ppm 10 : 1	94	67				
					8	I + IIa 3.75 + 3 ppm 1.25 : 1	99	78
35	10	I + IIb-1 7.5 + 0.75 ppm 10 : 1	44	0				
					40	11	I + IIb-1 3.75 + 0.375 ppm 10 : 1	56
12	I + IIb-1 3.75 + 3 ppm 1.25 : 1	61	44					

45 \*) efficacy calculated using Colby's formula

2003246634 03 Apr 2008

The test results show that for all mixing ratios the observed efficacy of the mixtures according to the invention is considerably higher than that predicted using Colby's formula.

5 Comprises/comprising and grammatical variations thereof when used in this specification are to be taken to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

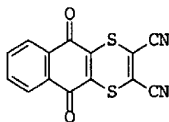
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We claim:

1. A fungicidal mixture, comprising

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- A) the compound of the formula I



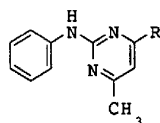
I

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and

- B) a pyrimidine derivative of the formula II,

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II

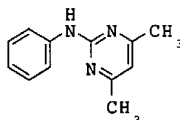
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in which R is methyl, cyclopropyl or 1-propynyl,

in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, comprising, as pyrimidine derivative II, the compound II-1.

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II-1

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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.

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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 to be kept free from them with the compound of the formula I and a compound of the formula II as set forth in claim 1.

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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

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from 5 to 2000 g/ha of the compound I 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 them with from 5 to 500 g/ha of at least one compound II as set forth in claim 1.
- 10 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.

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