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DESCRIPTION

[0001] The present invention relates to novel fungicidal compositions for the treatment of phytopathogenic diseases of useful plants, especially phytopathogenic fungi, and to a method of controlling phytopathogenic diseases on useful plants.

[0002] It is known from WO 2010/063700, WO 2010/084078 and WO 2008/151828 that certain pyrazolyl-carboxamide derivatives have biological activity against phytopathogenic fungi. On the other hand various fungicidal compounds of different chemical classes are widely known as plant fungicides for application in various crops of cultivated plants. However, crop tolerance and activity against phytopathogenic plant fungi do not always satisfy the needs of agricultural practice in many incidents and aspects.

[0003] There is therefore proposed in accordance with the present invention a method of controlling phytopathogenic diseases on useful plants or on propagation material thereof, which comprises applying to the useful plants, the locus thereof or propagation material thereof a combination of components (A) and (B), in a synergistically effective amount, wherein component (A) is 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide
and agrochemically acceptable salts/isomers/structural isomers/stereoisomers/diastereoisomers/enantiomers/tautomers and N-oxides of this compound;
and component (B) is a compound selected from the group consisting of

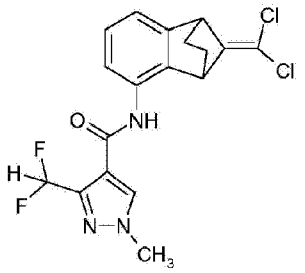
(B1) a strobilurin fungicide,

(B2) an azole fungicide,

(B3) an anilino-pyrimidine fungicide slected from the group consisting of cyprodinil, mepanipyrim and pyrimethanil;

(B4) the fungicide fluazinam,

(B5) isopyrazam, and the compound of formula (VII)



(VII).

[0004] Preferably component (B) is a compound selected from the group consisting of

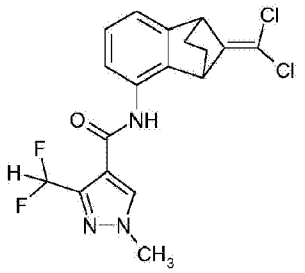
(B1) a strobilurin fungicide,

(B2) an azole fungicide,

(B3) an aniline-pyrimidine fungicide, selected from the group consisting of cyprodiinil, mapnipyrim and pyrimethanil,

(B4) the fungicide fluazinam,

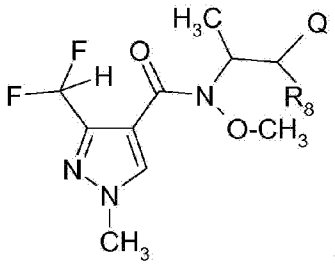
(B5) isopyrazam, and the compound of formula (VII)



(VII).

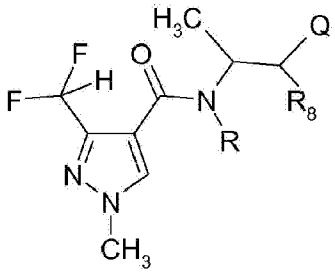
[0005] According to the instant invention, a "racemic compound" means a mixture of at least two enantiomers in a ratio of substantially 50 : 50.

[0006] Component (A) is a compound of formula (Ic) denoted as compound 1.001 in Table 1 below.



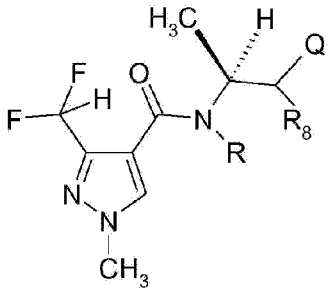
(Ic).

[0007] Formula (Ic) is a compound of formula I

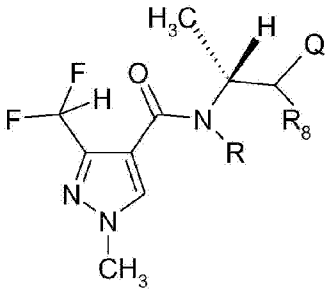


wherein R is O-CH_3.

[0008] The compounds of formula I can occur in the two enantiomeric forms of formula Ia and Ib:



(Ia) and



(Ib).

The invention encompasses both enantiomeric forms of component A. The compounds of formula I and their preparation are described in WO 2010/063700, WO 2010/084078 and WO 2008/151828.

[0009] It has been found that the use of component (B) in combination with component (A) surprisingly and substantially may enhance the effectiveness of the latter against fungi, and vice versa. Additionally, the method of the invention is effective against a wider spectrum of such fungi that can be combated with the active ingredients of this method, when used solely.

[0010] In general, the weight ratio of component (A) to component (B) is from 2000 : 1 to 1 : 1000. A non-limiting example for such weight ratios is compound of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide: compound of formula B-2 is 10:1. The weight ratio of component (A) to component (B) is preferably from 100 : 1 to 1 : 100; more preferably from 20 : 1 to 1 : 50.

[0011] The active ingredient mixture of component (A) to component (B) comprises 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide and a further, other biocidally active ingredient or composition preferably in a mixing ratio of from 1000:1 to 1:1000, especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are understood to include, on the one hand, ratios by weight and also, on other hand, molar ratios.

[0012] It has been found, surprisingly, that certain weight ratios of component (A) to component (B) are able to give rise to synergistic activity. Therefore, a further aspect of the invention are compositions, wherein component (A) and component (B) are present in the composition in amounts producing a synergistic effect. This synergistic activity is apparent from the fact that the fungicidal activity of the composition comprising component (A) and component (B) is greater than the sum of the fungicidal activities of component (A) and of component (B). This synergistic activity extends the range of action of component (A) and component (B) in two ways. Firstly, the rates of application of component (A) and component (B) are lowered whilst the action remains equally good, meaning that the active ingredient

mixture still achieves a high degree of phytopathogen control even where the two individual components have become totally ineffective in such a low application rate range. Secondly, there is a substantial broadening of the spectrum of phytopathogens that can be controlled.

[0013] A synergistic effect exists whenever the action of an active ingredient combination is greater than the sum of the actions of the individual components. The action to be expected E for a given active ingredient combination obeys the so-called COLBY formula and can be calculated as follows (COLBY, S.R. "Calculating synergistic and antagonistic responses of herbicide combination". Weeds, Vol. 15, pages 20-22; 1967):

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

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

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

[0014] According to COLBY, the expected (additive) action of active ingredients (A)+(B) using p+q ppm of active ingredient is

$$E = X + Y - \frac{X \cdot Y}{100}$$

If the action actually observed (O) is greater than the expected action (E), then the action of the combination is super-additive, i.e. there is a synergistic effect. In mathematical terms, synergism corresponds to a positive value for the difference of (O-E). In the case of purely complementary addition of activities (expected activity), said difference (O-E) is zero. A negative value of said difference (O-E) signals a loss of activity compared to the expected activity.

[0015] However, besides the actual synergistic action with respect to fungicidal activity, the compositions according to the invention can also have further surprising advantageous properties. Examples of such advantageous properties that may be mentioned are: more advantageuos degradability; improved toxicological and/or ecotoxicological behaviour; or improved characteristics of the useful plants including: emergence, crop yields, more developed root system, tillering increase, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf colour, less fertilizers needed, less seeds needed, more productive tillers, earlier flowering, early grain maturity, less plant verse (lodging), increased shoot growth, improved plant vigor, and early germination.

[0016] Some compositions according to the invention have a systemic action and can be used as foliar, soil and seed treatment fungicides.

[0017] With the compositions according to the invention it is possible to inhibit or destroy the phytopathogenic microorganisms which occur in plants or in parts of plants (fruit, blossoms, leaves, stems, tubers, roots) in different useful plants, while at the same time the parts of plants which grow later are also protected from attack by phytopathogenic microorganisms.

[0018] The compositions according to the invention can be applied to the phytopathogenic microorganisms, the useful plants, the locus thereof, the propagation material thereof, storage goods or technical materials threatened by microorganism attack.

[0019] The compositions according to the invention may be applied before or after infection of the useful plants, the propagation material thereof, storage goods or technical materials by the microorganisms.

[0020] A further aspect of the present invention is a method of controlling diseases on useful plants or on propagation material thereof caused by phytopathogens, which comprises applying to the useful plants, the locus thereof or propagation material thereof a composition according to the invention. Preferred is a method, which comprises applying to the useful plants or to the locus thereof a composition according to the invention, more preferably to the useful plants. Further preferred is a method, which comprises applying to the propagation material of the useful plants a composition according to the invention.

[0021] The components (B) are known. Where the components (B) are included in "The Pesticide Manual" [The Pesticide Manual - A World Compendium; Thirteenth Edition; Editor: C. D. S. Tomlin; The British Crop Protection Council], they are described therein under the entry number given in round brackets hereinabove for the particular component (B); for example, the compound "abamectin" is described under entry number (1). Most of the components (B) are referred to hereinabove by a so-called "common name", the relevant "ISO common name" or another "common name" being used in individual cases. If the designation is not a "common name", the nature of the designation used instead is given in round brackets for the particular component (B); in that case, the IUPAC name, the IUPAC/Chemical Abstracts name, a "chemical name", a "traditional name", a "compound name" or a "develoment code" is used or, if neither one of those designations nor a "common name" is used, an "alternative name" is employed.

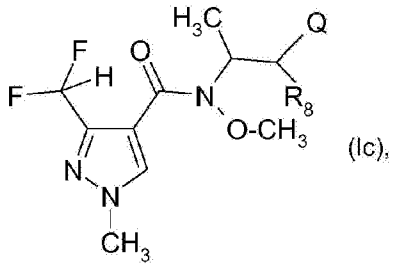
[0022] Throughout this document the expression "composition" stands for the various mixtures or combinations of components (A) and (B), for example in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the components (A) and (B) is not essential for working the present invention.

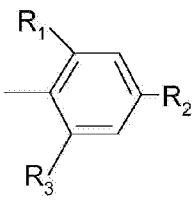
[0023] The compositions according to the invention may also comprise more than one of the active components (B), if, for example, a broadening of the spectrum of disease control is desired. For instance, it may be advantageous in the agricultural practice to combine two or three components (B) with component (A). An example is a composition comprising a 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide, azoxystrobin and cyproconazole.

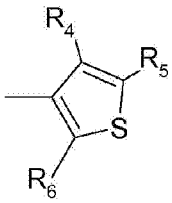
[0024] Component (A) is a compound of formula (Ic) denoted as compound 1.001 in Table 1 below:

Table 1: Compounds of formula Ic:

wherein Q is


(Ic),


(Q1) or


(Q2);

Compound No.	R_1	R_2	R_3	Q	R_4	R_5	R_6	R_8
1.001	Cl	Cl	Cl	Q_1	-	-	-	H
1.002	Cl	H	Cl	Q_1	-	-	-	H
1.003	Cl	Cl	H	Q_1	-	-	-	H
1.004	Cl	Br	Cl	Q_1	-	-	-	H
1.005	Br	Br	Br	Q_1	-	-	-	H
1.006	H	Cl	H	Q_1	-	-	-	H
1.007	H	Br	H	Q_1	-	-	-	H
1.008	H	CF_3	H	Q_1	-	-	-	H
1.009	-	-	-	Q_2	Cl	Cl	Cl	H
1.010	-	-	-	Q_2	Cl	H	Cl	H
1.011	-	-	-	Q_2	H	Cl	Cl	H
1.012	-	-	-	Q_2	Cl	Cl	Br	H
1.013	-	-	-	Q_2	Cl	H	Br	H
1.014	-	-	-	Q_2	H	Cl	Br	H
1.015	-	-	-	Q_2	H	Cl	H	H
1.016	-	-	-	Q_2	Cl	H	H	H
1.017	Cl	Cl	Cl	Q_1	-	-	-	OCH_3
1.018	Cl	H	Cl	Q_1	-	-	-	OCH_3

Compound No.	R_1	R_2	R_3	Q	R_4	R_5	R_6	R_8
1.019	Cl	Cl	H	Q_1	-	-	-	OCH_3
1.020	Cl	Br	Cl	Q_1	-	-	-	OCH_3
1.021	Br	Br	Br	Q_1	-	-	-	OCH_3
1.022	H	Cl	H	Q_1	-	-	-	OCH_3
1.023	H	Br	H	Q_1	-	-	-	OCH_3
1.024	H	CF_3	H	Q_1	-	-	-	OCH_3
1.025	-	-	-	Q_2	Cl	Cl	Cl	OCH_3
1.026	-	-	-	Q_2	Cl	H	Cl	OCH_3
1.027	-	-	-	Q_2	H	Cl	Cl	OCH_3
1.028	-	-	-	Q_2	Cl	Cl	Br	OCH_3
1.029	-	-	-	Q_2	Cl	H	Br	OCH_3
1.030	-	-	-	Q_2	H	Cl	Br	OCH_3
1.031	-	-	-	Q_2	H	Cl	H	OCH_3
1.032	-	-	-	Q_2	Cl	H	H	OCH_3

[0025] Described herein are compounds of formula (Ic) with preferred components (B). The abbreviation "TX" means: "one compound selected from the group consisting of the compounds specifically described in Table 1:

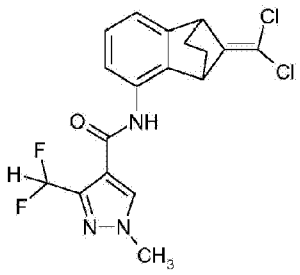
(B1) a strobilurin fungicide + TX,

(B2) an azole fungicide + TX,

(B3) an anilinopyrimidine fungicide + TX,

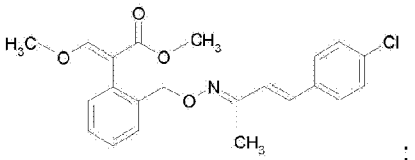
(B4) the fungicide fluazinam + TX,

(B5) isopyrazam + TX, and a compound of formula (VII) + TX



(VII).

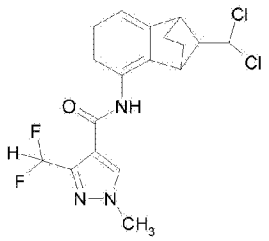
[0026] Specific mixtures described herein include a strobilurin fungicide selected from the group consisting of azoxystrobin + TX, dimoxystrobin + TX, fluoxastrobin + TX, kresoxim-methyl + TX, metominostrobin + TX, orysastrobin + TX, picoxystrobin + TX, pyraclostrobin; trifloxystrobin and a compound of formula B-1.1



;

an azole fungicide selected from the group consisting of azaconazole + TX, bromuconazole + TX, cyproconazole + TX, difenoconazole + TX, diniconazole + TX, diniconazole-M + TX, epoxiconazole + TX, fenbuconazole + TX, fluquinconazole + TX, flusilazole + TX, flutriafol + TX, hexaconazole + TX, imazalil + TX, imibenconazole + TX, ipconazole + TX, metconazole + TX, myclobutanil + TX, oxpoconazole + TX, pefurazoate + TX, penconazole + TX, prochloraz + TX, propiconazole + TX, prothioconazole + TX, simeconazole + TX, tebuconazole + TX, tetraconazole + TX, triadimefon + TX, triadimenol + TX, triflumizole + TX, triticonazole + TX, diclobutrazol + TX, etaconazole + TX, furconazole + TX, furconazole-cis and quinconazole;
an anilino-pyrimidine fungicide selected from the group consisting of cyprodinil + TX, mepanipyrim and pyrimethanil;
a fungicide selected from the group consisting of

(B5) isopyrazam + TX, and a compound of formula (VII) + TX



(VII).

[0027] The active ingredient combinations are effective against harmful microorganisms, such as microorganisms, that cause phytopathogenic diseases, in particular against phytopathogenic fungi and bacteria.

[0028] The active ingredient combinations are effective especially against phytopathogenic fungi belonging to the following classes: Ascomycetes (e.g. Venturia, Podosphaera, Erysiphe, Monilinia, Mycosphaerella, Uncinula); Basidiomycetes (e.g. the genus Hemileia, Rhizoctonia, Phakopsora, Puccinia, Ustilago, Tilletia); Fungi imperfecti (also known as Deuteromycetes; e.g. Botrytis, Helminthosporium, Rhynchosporium, Fusarium, Septoria, Cercospora, Alternaria, Pyricularia and Pseudocercosporella); Oomycetes (e.g. Phytophthora, Peronospora, Pseudoperonospora, Albugo, Bremia, Pythium, Pseudosclerospora, Plasmopara).

[0029] According to the invention "useful plants" typically comprise the following species of plants: grape vines; cereals, such as wheat, barley, rye or oats; beet, such as sugar beet or

fodder beet; fruits, such as pomes, stone fruits or soft fruits, for example apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries or blackberries; leguminous plants, such as beans, lentils, peas or soybeans; oil plants, such as rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans or groundnuts; cucumber plants, such as marrows, cucumbers or melons; fibre plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruit or mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceae, such as avocados, cinnamon or camphor; maize; tobacco; nuts; coffee; sugar cane; tea; vines; hops; durian; bananas; natural rubber plants; turf or ornamentals, such as flowers, shrubs, broad-leaved trees or evergreens, for example conifers. This list does not represent any limitation.

[0030] The term "useful plants" is to be understood as including also useful plants that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides (such as, for example, HPPD inhibitors, ALS inhibitors, for example primisulfuron, prosulfuron and trifloxysulfuron, EPSPS (5-enol-pyrovyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine synthetase) inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering methods include glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® , Herculex I® and LibertyLink®.

[0031] The term "useful plants" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the genus Bacillus.

[0032] Toxins that can be expressed by such transgenic plants include, for example, insecticidal proteins, for example insecticidal proteins from Bacillus cereus or Bacillus popliae; or insecticidal proteins from Bacillus thuringiensis, such as δ-endotoxins, e.g. CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) or Cry9c, or vegetative insecticidal proteins (VIP), e.g. VIP1, VIP2, VIP3 or VIP3A; or insecticidal proteins of bacteria colonising nematodes, for example Photorhabdus spp. or Xenorhabdus spp., such as Photorhabdus luminescens, Xenorhabdus nematophilus; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins and other insect-specific neurotoxins; toxins produced by fungi, such as Streptomycetes toxins, plant lectins, such as pea lectins, barley lectins or snowdrop lectins; agglutinins; proteinase inhibitors, such as trypsine inhibitors, serine protease inhibitors, patatin, cystatin, papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 3-hydroxysteroidoxidase, ecdysteroid-UDP-glycosyl-transferase, cholesterol oxidases, ecdysone inhibitors, HMG-COA-reductase, ion channel blockers, such as blockers of sodium or calcium channels, juvenile hormone esterase, diuretic hormone receptors, stilbene synthase, bibenzyl

synthase, chitinases and glucanases.

[0033] In the context of the present invention there are to be understood by δ-endotoxins, for example CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) or Cry9c, or vegetative insecticidal proteins (VIP), for example VIP1, VIP2, VIP3 or VIP3A, expressly also hybrid toxins, truncated toxins and modified toxins. Hybrid toxins are produced recombinantly by a new combination of different domains of those proteins (see, for example, WO 02/15701). An example for a truncated toxin is a truncated CryIA(b), which is expressed in the Bt11 maize from Syngenta Seed SAS, as described below. In the case of modified toxins, one or more amino acids of the naturally occurring toxin are replaced. In such amino acid replacements, preferably non-naturally present protease recognition sequences are inserted into the toxin, such as, for example, in the case of CryIIIA055, a cathepsin-D-recognition sequence is inserted into a CryIIIA toxin (see WO 03/018810)

[0034] Examples of such toxins or transgenic plants capable of synthesising such toxins are disclosed, for example, in EP-A-0 374 753, WO 93/07278, WO 95/34656, EP-A-0 427 529, EP-A-451 878 and WO 03/052073.

[0035] The processes for the preparation of such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above. Cryl-type deoxyribonucleic acids and their preparation are known, for example, from WO 95/34656, EP-A-0 367 474, EP-A-0 401 979 and WO 90/13651.

[0036] The toxin contained in the transgenic plants imparts to the plants tolerance to harmful insects. Such insects can occur in any taxonomic group of insects, but are especially commonly found in the beetles (Coleoptera), two-winged insects (Diptera) and butterflies (Lepidoptera).

[0037] Transgenic plants containing one or more genes that code for an insecticidal resistance and express one or more toxins are known and some of them are commercially available. Examples of such plants are: YieldGard® (maize variety that expresses a CryIA(b) toxin); YieldGard Rootworm® (maize variety that expresses a CryIIIB(b1) toxin); YieldGard Plus® (maize variety that expresses a CryIA(b) and a CryIIIB(b1) toxin); Starlink® (maize variety that expresses a Cry9(c) toxin); Herculex I® (maize variety that expresses a CryIF(a2) toxin and the enzyme phosphinothricine N-acetyltransferase (PAT) to achieve tolerance to the herbicide glufosinate ammonium); NuCOTN 33B® (cotton variety that expresses a CryIA(c) toxin); Bollgard I® (cotton variety that expresses a CryIA(c) toxin); Bollgard II® (cotton variety that expresses a CryIA(c) and a CryIIA(b) toxin); VIPCOT® (cotton variety that expresses a VIP toxin); NewLeaf® (potato variety that expresses a CryIIIA toxin); Nature-Gard® and Protecta®.

[0038] Further examples of such transgenic crops are:

1. 1. **Bt11 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified *Zea mays* which has

been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a truncated CryIA(b) toxin. Bt11 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.

2. 2. **Bt176 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Genetically modified Zea *mays* which has been rendered resistant to attack by the European corn borer (*Ostrinia nubilalis* and *Sesamia nonagrioides*) by transgenic expression of a CryIA(b) toxin. Bt176 maize also transgenically expresses the enzyme PAT to achieve tolerance to the herbicide glufosinate ammonium.
3. 3. **MIR604 Maize** from Syngenta Seeds SAS, Chemin de l'Hobit 27, F-31 790 St. Sauveur, France, registration number C/FR/96/05/10. Maize which has been rendered insect-resistant by transgenic expression of a modified CryIIIA toxin. This toxin is Cry3A055 modified by insertion of a cathepsin-D-protease recognition sequence. The preparation of such transgenic maize plants is described in WO 03/018810.
4. 4. **MON 863 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/DE/02/9. MON 863 expresses a CryIIIB(b1) toxin and has resistance to certain Coleoptera insects.
5. 5. **IPC 531 Cotton** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/ES/96/02.
6. **6. 1507 Maize** from Pioneer Overseas Corporation, Avenue Tedesco, 7 B-1160 Brussels, Belgium, registration number C/NL/00/10. Genetically modified maize for the expression of the protein Cry1F for achieving resistance to certain Lepidoptera insects and of the PAT protein for achieving tolerance to the herbicide glufosinate ammonium.
7. 7. **NK603 × MON 810 Maize** from Monsanto Europe S.A. 270-272 Avenue de Tervuren, B-1150 Brussels, Belgium, registration number C/GB/02/M3/03. Consists of conventionally bred hybrid maize varieties by crossing the genetically modified varieties NK603 and MON 810. NK603 × MON 810 Maize transgenically expresses the protein CP4 EPSPS, obtained from *Agrobacterium sp.* strain CP4, which imparts tolerance to the herbicide Roundup® (contains glyphosate), and also a CryIA(b) toxin obtained from *Bacillus thuringiensis subsp. kurstaki* which brings about tolerance to certain Lepidoptera, include the European corn borer.

Transgenic crops of insect-resistant plants are also described in BATS (Zentrum fur Biosicherheit und Nachhaltigkeit, Zentrum BATS, Clarastrasse 13, 4058 Basel, Switzerland) Report 2003, (http://bats.ch).

[0039] The term "useful plants" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818, and EP-A-0 353 191. The methods of producing such transgenic plants are generally known to the person

skilled in the art and are described, for example, in the publications mentioned above.

[0040] Antipathogenic substances which can be expressed by such transgenic plants include, for example, ion channel blockers, such as blockers for sodium and calcium channels, for example the viral KP1, KP4 or KP6 toxins; stilbene synthases; bibenzyl synthases; chitinases; glucanases; the so-called "pathogenesis-related proteins" (PRPs; see e.g. EP-A-0 392 225); antipathogenic substances produced by microorganisms, for example peptide antibiotics or heterocyclic antibiotics (see e.g. WO 95/33818) or protein or polypeptide factors involved in plant pathogen defence (so-called "plant disease resistance genes", as described in WO 03/000906).

[0041] Useful plants of elevated interest in connection with present invention are cereals; soybean; rice; oil seed rape; pome fruits; stone fruits; peanuts; coffee; tea; strawberries; turf; vines and vegetables, such as tomatoes, potatoes, cucurbits and lettuce.

[0042] The term "locus" of a useful plant as used herein is intended to embrace the place on which the useful plants are growing, where the plant propagation materials of the useful plants are sown or where the plant propagation materials of the useful plants will be placed into the soil. An example for such a locus is a field, on which crop plants are growing.

[0043] The term "plant propagation material" is understood to denote generative parts of a plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected before transplantation by a total or partial treatment by immersion. Preferably "plant propagation material" is understood to denote seeds.

[0044] A futher aspect of the instant invention is a method of protecting natural substances of plant and/or animal origin, which have been taken from the natural life cycle, and/or their processed forms against attack of fungi, which comprises applying to said natural substances of plant and/or animal origin or their processed forms a combination of components (A) and (B) in a synergistically effective amount, with the proviso that said application of the combination of components (A) and (B) does not constitute application to the body of a live animal.

[0045] According to the instant invention, the term "natural substances of plant origin, which have been taken from the natural life cycle" denotes plants or parts thereof which have been harvested from the natural life cycle and which are in the freshly harvested form. Examples of such natural substances of plant origin are stalks, leafs, tubers, seeds, fruits or grains. According to the instant invention, the term "processed form of a natural substance of plant origin" is understood to denote a form of a natural substance of plant origin that is the result of a modification process. Such modification processes can be used to transform the natural substance of plant origin in a more storable form of such a substance (a storage good).

Examples of such modification processes are pre-drying, moistening, crushing, comminuting, grounding, compressing or roasting. Also falling under the definition of a processed form of a natural substance of plant origin is timber, whether in the form of crude timber, such as construction timber, electricity pylons and barriers, or in the form of finished articles, such as furniture or objects made from wood.

[0046] According to the instant invention, the term "natural substances of animal origin, which have been taken from the natural life cycle and/or their processed forms" is understood to denote material of animal origin such as skin, hides, leather, furs, hairs and the like.

[0047] The combinations according the present invention can prevent disadvantageous effects such as decay, discoloration or mold.

[0048] A preferred embodiment is a method of protecting natural substances of plant origin, which have been taken from the natural life cycle, and/or their processed forms against attack of fungi, which comprises applying to said natural substances of plant and/or animal origin or their processed forms a combination of components (A) and (B) in a synergistically effective amount.

[0049] A further preferred embodiment is a method of protecting fruits, preferably pomes, stone fruits, soft fruits and citrus fruits, which have been taken from the natural life cycle, and/or their processed forms, which comprises applying to said fruits and/or their processed forms a combination of components (A) and (B) in a synergistically effective amount.

[0050] The combinations of the present invention may also be used in the field of protecting industrial material against attack of fungi. According to the instant invention, the term "industrial material" denotes non-live material which have been prepared for use in industry. For example, industrial materials which are intended to be protected against attack of fungi can be glues, sizes, paper, board, textiles, carpets, leather, wood, constructions, paints, plastic articles, cooling lubricants, aquaeous hydraulic fluids and other materials which can be infested with, or decomposed by, microorganisms. Cooling and heating systems, ventilation and air conditioning systems and parts of production plants, for example cooling-water circuits, which may be impaired by multiplication of microorganisms may also be mentioned from amongst the materials to be protected. The combinations according the present invention can prevent disadvantageous effects such as decay, discoloration or mold.

[0051] The combinations of the present invention may also be used in the field of protecting technical material against attack of fungi. According to the instant invention, the term "technical material" includes paper; carpets; constructions; cooling and heating systems; ventilation and air conditioning systems and the like. The combinations according the present invention can prevent disadvantageous effects such as decay, discoloration or mold.

[0052] The combinations according to the present invention are particularly effective against powdery mildews; rusts; leafspot species; early blights and molds; especially against Septoria,

Puccinia, Erysiphe, Pyrenophora and Tapesia in cereals; Phakopsora in soybeans; Hemileia in coffee; Phragmidium in roses; Alternaria in potatoes, tomatoes and cucurbits; Sclerotinia in turf, vegetables, sunflower and oil seed rape; black rot, red fire, powdery mildew, grey mold and dead arm disease in vine; Botrytis cinerea in fruits; Monilinia spp. in fruits and Penicillium spp. in fruits.

The combinations according to the present invention are furthermore particularly effective against seedborne and soilborne diseases, such as Alternaria spp., Ascochyta spp., Botrytis cinerea, Cercospora spp., Claviceps purpurea, Cochliobolus sativus, Colletotrichum spp., Epicoccum spp., Fusarium graminearum, Fusarium moniliforme, Fusarium oxysporum, Fusarium proliferatum, Fusarium solani, Fusarium subglutinans, Gäumannomyces graminis , Helminthosporium spp., Microdochium nivale, Phoma spp., Pyrenophora graminea, Pyricularia oryzae, Rhizoctonia solani, Rhizoctonia cerealis, Sclerotinia spp., Septoria spp., Sphacelotheca reilliana, Tilletia spp., Typhula incarnata, Urocystis occulta, Ustilago spp. or Verticillium spp.; in particular against pathogens of cereals, such as wheat, barley, rye or oats; maize; rice; cotton; soybean; turf; sugarbeet; oil seed rape; potatoes; pulse crops, such as peas, lentils or chickpea; and sunflower.

The combinations according to the present invention are furthermore particularly effective against post harvest diseasese such as Botrytis cinerea, Colletotrichum musae, Curvularia lunata, Fusarium semitecum, Geotrichum candidum, Monilinia fructicola, Monilinia fructigena, Monilinia laxa, Mucor piriformis, Penicilium italicum, Penicilium solitum, Penicillium digitatum or Penicillium expansum in particular against pathogens of fruits, such as pomefruits, for example apples and pears, stone fruits, for example peaches and plums, citrus, melons, papaya, kiwi, mango, berries, for example strawberries, avocados, pomegranates and bananas, and nuts.

[0053] The amount of a combination of the invention to be applied, will depend on various factors, such as the compounds employed; the subject of the treatment, such as, for example plants, soil or seeds; the type of treatment, such as, for example spraying, dusting or seed dressing; the purpose of the treatment, such as, for example prophylactic or therapeutic; the type of fungi to be controlled or the application time.

[0054] It has been found that the use of components (B) in combination with 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide surprisingly and substantially enhance the effectiveness of the latter against fungi, and vice versa. Additionally, the method of the invention is effective against a wider spectrum of such fungi that can be combated with the active ingredients of this method, when used solely.

[0055] The active ingredient mixture of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide with active ingredients (B) described above comprises 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide and an active ingredient as described above preferably in a mixing ratio of from 1000:1 to 1:1000, especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3,

or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are understood to include, on the one hand, ratios by weight and also, on other hand, molar ratios.

[0056] The mixtures of the invention as described above can be applied, for example, in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying components A and B is not essential for working the present invention.

[0057] The synergistic activity of the combination is apparent from the fact that the fungicidal activity of the composition of (A) + (B) is greater than the sum of the fungicidal activities of (A) and (B).

[0058] The method of the invention comprises applying to the useful plants, the locus thereof or propagation material thereof in admixture or separately, a synergistically effective aggregate amount of a component (A) and a component (B).

[0059] Some of said combinations according to the invention have a systemic action and can be used as foliar, soil and seed treatment fungicides.

[0060] With the combinations according to the invention it is possible to inhibit or destroy the phytopathogenic microorganisms which occur in plants or in parts of plants (fruit, blossoms, leaves, stems, tubers, roots) in different useful plants, while at the same time the parts of plants which grow later are also protected from attack by phytopathogenic microorganisms.

[0061] The combinations of the present invention are of particular interest for controlling a large number of fungi in various useful plants or their seeds, especially in field crops such as potatoes, tobacco and sugarbeets, and wheat, rye, barley, oats, rice, maize, lawns, cotton, soybeans, oil seed rape, pulse crops, sunflower, coffee, sugarcane, fruit and ornamentals in horticulture and viticulture, in vegetables such as cucumbers, beans and cucurbits.

[0062] The combinations according to the invention are applied by treating the fungi, the useful plants, the locus thereof, the propagation material thereof, the natural substances of plant and/or animal origin, which have been taken from the natural life cycle, and/or their processed forms, or the industrial materials threatened by fungus attack with a combination of components (A) and (B) in a synergistically effective amount.

[0063] The combinations according to the invention may be applied before or after infection of the useful plants, the propagation material thereof, the natural substances of plant and/or animal origin, which have been taken from the natural life cycle, and/or their processed forms,

or the industrial materials by the fungi.

[0064] The combinations according to the invention are particularly useful for controlling the following plant diseases:

Alternaria species in fruit and vegetables,

Ascochyta species in pulse crops,

Botrytis cinerea in strawberries, tomatoes, sunflower, pulse crops, vegetables and grapes,

Cercospora arachidicola in peanuts,

Cochliobolus sativus in cereals,

Colletotrichum species in pulse crops,

Erysiphe species in cereals,

Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits,

Fusarium species in cereals and maize,

Gäumannomyces graminis in cereals and lawns,

Helminthosporium species in maize, rice and potatoes,

Hemileia vastatrix on coffee,

Microdochium species in wheat and rye,

Phakopsora species in soybean,

Puccinia species in cereals, broadleaf crops and perrenial plants,

Pseudocercosporella species in cereals,

Phragmidium mucronatum in roses,

Podosphaera species in fruits,

Pyrenophora species in barley,

Pyricularia oryzae in rice,

Ramularia collo-cygni in barley,

Rhizoctonia species in cotton, soybean, cereals, maize, potatoes, rice and lawns,

Rhynchosporium secalis in barley and rye,

Sclerotinia species in lawns, lettuce, vegetables and oil seed rape,

Septoria species in cereals, soybean and vegetables,

Sphacelotheca reilliana in maize,

Tilletia species in cereals,

Uncinula necator, Guignardia bidwellii and Phomopsis viticola in vines,

Urocystis occulta in rye,

Ustilago species in cereals and maize,

Venturia species in fruits,

Monilinia species on fruits,

Penicillium species on citrus and apples.

[0065] The combinations according to the invention are preventively and/or curatively valuable active ingredients in the field of pest control, even at low rates of application, which have a very favorable biocidal spectrum and are well tolerated by warm-blooded species, fish and plants. The active ingredients according to the invention which are partially known for their insecticidal action act against all or individual developmental stages of normally sensitive, but also resistant, animal pests, such as insects or representatives of the order Acarina. The insecticidal or acaricidal activity of the combinations according to the invention can manifest itself directly, i.e. in destruction of the pests, which takes place either immediately or only after some time has elapsed, for example during ecdysis, or indirectly, for example in a reduced oviposition and/or hatching rate, a good activity corresponding to a destruction rate (mortality) of at least 50 to 60%.

[0066] Examples of the abovementioned animal pests are:

from the order *Acarina,* for example,

Acarus siro, Aceria sheldoni, Aculus schlechtendali, Amblyomma spp., Argas spp., Boophi-lus spp., Brevipalpus spp., Bryobia praetiosa, Calipitrimerus spp., Chorioptes spp., Derma-nyssus gallinae, Eotetranychus carpini, Eriophyes spp., Hyalomma spp., Ixodes spp., Oly-gonychus pratensis, Ornithodoros spp., Panonychus spp., Phyllocoptruta oleivora, Polypha-gotarsonemus latus, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Tarsonemus spp. and Tetranychus spp.;

from the order *Anoplura,* for example,

Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.;

from the order *Coleoptera,* for example,

Agriotes spp., Anthonomus spp., Atomaria linearis, Chaetocnema tibialis, Cosmopolites spp., Curculio spp., Dermestes spp., Diabrotica spp., Epilachna spp., Eremnus spp., Leptinotarsa decemlineata, Lissorhoptrus spp., Melolontha spp., Orycaephilus spp., Otiorhynchus spp., Phlyctinus spp., Popillia spp., Psylliodes spp., Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Tenebrio spp., Tribolium spp. and Trogoderma spp.;

from the order *Diptera,* for example,

Aedes spp., Antherigona soccata, Bibio hortulanus, Calliphora erythrocephala, Ceratitis spp., Chrysomyia spp., Culex spp., Cuterebra spp., Dacus spp., Drosophila melanogaster, Fannia spp., Gastrophilus spp., Glossina spp., Hypoderma spp., Hyppobosca spp., Liriomyza spp., Lucilia spp., Melanagromyza spp., Musca spp., Oestrus spp., Orseolia spp., Oscinella frit, Pegomyia hyoscyami, Phorbia spp., Rhagoletis pomonella, Sciara spp., Stomoxys spp., Tabanus spp., Tannia spp. and Tipula spp.;

from the order *Heteroptera,* for example,

Cimex spp., Distantiella theobroma, Dysdercus spp., Euchistus spp., Eurygaster spp., Leptocorisa spp., Nezara spp., Piesma spp., Rhodnius spp., Sahlbergella singularis, Scotinophara spp. and Triatoma spp.;

from the order *Homoptera,* for example,

Aleurothrixus floccosus, Aleyrodes brassicae, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Bemisia tabaci, Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Coccus hesperidum, Empoasca spp., Eriosoma larigerum, Erythroneura spp., Gascardia spp., Laodelphax spp., Lecanium corni, Lepidosaphes spp., Macrosiphus spp., Myzus spp., Nephotettix spp., Nilaparvata spp., Parlatoria spp., Pemphigus spp., Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Psylla spp., Pulvinaria aethiopica, Quadraspidiotus spp., Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Trialeurodes vaporariorum, Trioza erytreae and Unaspis citri;

from the order *Hymenoptera,* for example,

Acromyrmex, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Solenopsis spp. and Vespa spp.;

from the order *Isoptera,* for example,

Reticulitermes spp.;

from the order *Lepidoptera,* for example,

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyrotaenia spp., Autographa spp., Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Crocidolomia binotalis, Cryptophlebia leucotreta, Cydia spp., Diatraea spp., Diparopsis castanea, Earias spp.,

Ephestia spp., Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Operophtera spp., Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Pectinophora gossypiela, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni and Yponomeuta spp.;

from the order *Mallophaga,* for example,

Damalinea spp. and Trichodectes spp.;

from the order *Orthoptera,* for example,

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Periplaneta spp. and Schistocerca spp.;

from the order *Psocoptera,* for example,

Liposcelis spp.;

from the order *Siphonaptera,* for example,

Ceratophyllus spp., Ctenocephalides spp. and Xenopsylla cheopis;

from the order *Thysanoptera,* for example,

Frankliniella spp., Hercinothrips spp., Scirtothrips aurantii, Taeniothrips spp., Thrips palmi and Thrips tabaci;

from the order *Thysanura,* for example,

Lepisma saccharina;

nematodes, for example root knot nematodes, stem eelworms and foliar nematodes; especially Heterodera spp., for example Heterodera schachtii, Heterodora avenae and Heterodora trifolii; Globodera spp., for example Globodera rostochiensis; Meloidogyne spp., for example Meloidogyne incoginita and Meloidogyne javanica; Radopholus spp., for example Radopholus similis; Pratylenchus, for example Pratylenchus neglectans and Pratylenchus penetrans; Tylenchulus, for example Tylenchulus semipenetrans; Longidorus, Trichodorus, Xiphinema, Ditylenchus, Aphelenchoides and Anguina;

crucifer flea beetles (Phyllotreta spp.);

root maggots (Delia spp.) and

cabbage seedpod weevil (Ceutorhynchus spp.).

[0067] The combinations according to the invention can be used for controlling, i. e. containing or destroying, animal pests of the abovementioned type which occur on useful plants in agriculture, in horticulture and in forests, or on organs of useful plants, such as fruits, flowers, foliage, stalks, tubers or roots, and in some cases even on organs of useful plants which are formed at a later point in time remain protected against these animal pests.

[0068] When applied to the useful plants the compound 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide is applied at a rate of 5 to 2000 g a.i./ha, particularly 10 to 1000 g a.i./ha, e.g. 50, 75, 100 or 200 g a.i./ha, in association with 1 to 5000 g a.i./ha, particularly 2 to 2000 g a.i./ha, e.g. 100, 250, 500, 800, 1000, 1500 g a.i./ha of a compound of component (B), depending on the class of chemical employed as component (B).

[0069] In agricultural practice the application rates of the combination according to the invention depend on the type of effect desired, and typically range from 20 to 4000 g of total combination per hectare.

[0070] When the combinations of the present invention are used for treating seed, rates of 0.001 to 50 g of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide per kg of seed, preferably from 0.01 to 10g per kg of seed, and 0.001 to 50 g of a compound of component (B), per kg of seed, preferably from 0.01 to 10g per kg of seed, are generally sufficient.

[0071] The invention also provides fungicidal compositions comprising a combination of components (A) and (B) as mentioned above in a synergistically effective amount, together with an agriculturally acceptable carrier, and optionally a surfactant. In said compositions, the weight ratio of (A) to (B) is preferably between 1000 : 1 and 1 : 1000.

[0072] The compositions of the invention may be employed in any conventional form, for example in the form of a twin pack, a powder for dry seed treatment (DS), an emulsion for seed treatment (ES), a flowable concentrate for seed treatment (FS), a solution for seed treatment (LS), a water dispersible powder for seed treatment (WS), a capsule suspension for seed treatment (CF), a gel for seed treatment (GF), an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), an emulsion, water in oil (EO), an emulsion, oil in water (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a technical concentrate (TK), a dispersible concentrate (DC), a wettable powder (WP) or any technically feasible formulation in combination with agriculturally acceptable adjuvants.

[0073] Such compositions may be produced in conventional manner, e.g. by mixing the active ingredients with appropriate formulation inerts (diluents, solvents, fillers and optionally other

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

[0074] A seed dressing formulation is applied in a manner known per se to the seeds employing the combination of the invention and a diluent in suitable seed dressing formulation form, e.g. as an aqueous suspension or in a dry powder form having good adherence to the seeds. Such seed dressing formulations are known in the art. Seed dressing formulations may contain the single active ingredients or the combination of active ingredients in encapsulated form, e.g. as slow release capsules or microcapsules.

[0075] In general, the formulations include from 0.01 to 90% by weight of active agent, from 0 to 20% agriculturally acceptable surfactant and 10 to 99.99% solid or liquid formulation inerts and adjuvant(s), the active agent consisting of at least 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid methoxy-[1-methyl-2-(2,4,6-trichlorophenyl)-ethyl]-amide together with a compound of component (B), and optionally other active agents, particularly microbiocides or conservatives or the like. Concentrated forms of compositions generally contain in between about 2 and 80%, preferably between about 5 and 70% by weight of active agent. Application forms of formulation may for example contain from 0.01 to 20% by weight, preferably from 0.01 to 5% by weight of active agent. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ diluted formulations.

[0076] The Examples which follow serve to illustrate the invention, "active ingredient" denoting a mixture of component (A) and a compound of component (B) in a specific mixing ratio.

Formulation Examples

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

[0077] The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders that can be diluted with water to give suspensions of the desired concentration.

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

[0078] The active ingredient is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording powders that can be used directly for seed treatment.

Emulsifiable concentrate

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

[0079] Emulsions of any required dilution, which can be used in plant protection, can be obtained from this concentrate by dilution with water.

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

[0080] Ready-for-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill. Such powders can also be used for dry dressings for seed.

Extruder granules

Active ingredient (comp (A) : comp (B) = 2:1)	15 %
sodium lignosulfonate	2 %

carboxymethylcellulose	1 %
Kaolin	82 %

[0081] The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

Coated granules

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

[0082] The finely ground active ingredient is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

Suspension concentrate

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

[0083] The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

Flowable concentrate for seed treatment

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

[0084] The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

Slow Release Capsule Suspension

[0085] 28 parts of a combination of component (A) and a compound of component (B), or of each of these compounds separately, are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of 1.2 parts of polyvinylalcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed.

[0086] The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns.

[0087] The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

Biological Examples

[0088] A synergistic effect exists whenever the action of an active ingredient combination is greater than the sum of the actions of the individual components.

[0089] The action to be expected E for a given active ingredient combination obeys the so-called COLBY formula and can be calculated as follows (COLBY, S.R. "Calculating synergistic and antagonistic responses of herbicide combination". Weeds, Vol. 15, pages 20-22; 1967): ppm = milligrams of active ingredient (= a.i.) per liter of spray mixture X = % action by active ingredient (A) using p ppm of active ingredient Y = % action by active ingredient (B) using q ppm of active ingredient.

[0090] According to COLBY, the expected (additive) action of active ingredients (A)+(B) using p+q ppm of active ingredient is

$$E = X + Y - \frac{X \cdot Y}{100}$$

If the action actually observed (O) is greater than the expected action (E), then the action of the combination is super-additive, i.e. there is a synergistic effect. In mathematical terms the

synergism factor SF corresponds to O/E. In the agricultural practice an SF of ≥ 1.2 indicates significant improvement over the purely complementary addition of activities (expected activity), while an SF of ≤ 0.9 in the practical application routine signals a loss of activity compared to the expected activity.

Liquid culture tests in well plates:

[0091] Mycelia fragments or conidia suspensions of a fungus, prepared either freshly from liquid cultures of the fungus or from cryogenic storage, were directly mixed into nutrient broth. DMSO solutions of the test compound (max. 10 mg/ml) was diluted with 0.025% Tween20 by factor 50 and 10 µl of this solution was pipetted into a microtiter plate (96-well format). The nutrient broth containing the fungal spores/mycelia fragments was then added to give an end concentration of the tested compound. The test plates were incubated in the dark at 24°C and 96% rh. The inhibition of fungal growth was determined visually after 2 - 7 days, depending on the pathosystem, and percent antifungal activity relative to the untreated check was calculated.

Example B1: Fungicidal action against *Botryotinia fuckeliana* (*Botrytis cinerea*) / liquid culture (Gray mould)

[0092] Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (Vogels broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 3-4 days after application.

Example B2: Fungicidal action against *Pythium ultimum* / liquid culture (seedling damping off):

[0093] Mycelia fragments and oospores of a newly grown liquid culture of the fungus were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal mycelia/spore mixture was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 2-3 days after application.

Example B3: Fungicidal action against *Sclerotinia sclerotiorum* / liquid culture (cottony rot):

[0094] Mycelia fragments of a newly grown liquid culture of the fungus were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test

compounds into a microtiter plate (96-well format) the nutrient broth containing the fungal material was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 3-4 days after application.

Example B4: Fungicidal action against *Mycosphaerella arachidis* (*Cercospora arachidicola*) / liquid culture (early leaf spot)

[0095] Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 4-5 days after application.

Example B5: Fungicidal action against *Tapesia yallundae* *W-type (Pseudocercosporella herpotrichoides)* / liquid culture (eyespot):

[0096] Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 3-4 days after application.

Example B6: Fungicidal action against *Mycosphaerella graminicola (Septoria tritici)* / liquid culture (Septoria blotch) :

[0097] Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 4-5 days after application.

Example B7: Fungicidal action against *Fusarium culmorum* / liquid culture (Head blight):

[0098] Conidia of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal spores was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 3-

4 days after application.

Example B8 Fungicidal action against *Thanatephorus cucumeris (Rhizoctonia solani)* / liquid culture (foot rot, damping-off):

[0099] Mycelia fragments of a newly grown liquid culture of the fungus were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal material was added. The test plates were incubated at 24°C and the inhibition of growth was determined visually 3-4 days after application.

Leaf disk or leaf segment tests in well plates:

[0100] Leaf disks or leaf segments of various plant species were cut from plants grown in the greenhouse. The cut leaf disks or segments were placed in multiwell plates (24-well format) onto water agar. The leaf disks were sprayed with a test solution before (preventative) or after (curative) inoculation. Compounds to be tested were prepared as DMSO solutions (max. 10 mg/ml) which were diluted to the appropriate concentration with 0.025% Tween20 just before spraying. The inoculated leaf disks or segments were incubated under defined conditions (temperature, relative humidity, light, etc.) according to the respective test system. A single evaluation of disease level was carried out 3-9 days days after inoculation, depending on the pathosystem. Percent disease control relative to the untreated check leaf disks or segments was then calculated.

Example B9 Fungicidal action against *Plasmopara viticola* / grape / leaf disc preventative (late blight):

[0101] Grape vine leaf disks were placed on water agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks were inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf disks were incubated at 19°C and 80% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound was assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (6 - 8 days after application).

REFERENCES CITED IN THE DESCRIPTION

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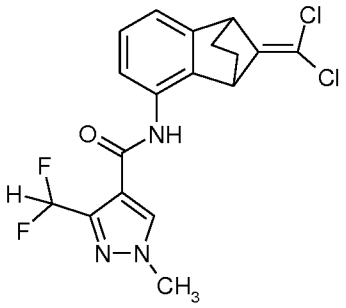
- **COLBY, S.R.**Calculating synergistic and antagonistic responses of herbicide combinationWeeds, 1967, vol. 15, 20-22 [0013] [0089]
- The Pesticide ManualThe Pesticide Manual - A World CompendiumThe British Crop Protection Council [0021]

Patentkrav

1. Fremgangsmåde til bekæmpelse af fytopatogene sygdomme på nytteplanter eller på opformeringsmateriale deraf, som omfatter påføring på nytteplanterne, voksestedet derfor eller opformeringsmaterialet deraf af en kombination af bestanddel (A) og (B) i en synergistisk effektiv mængde, hvor bestanddel (A) er 3-difluormethyl-1-methyl-1H-pyrazol-4-carboxylsyremethoxy-[1-methyl-2-(2,4,6-trichlorphenyl)-ethyl]-amid og agrokemisk acceptable salte/isomerer/strukturelle isomerer/stereoisomerer/diastereoisomerer/enantiomerer/tautomerer og N-oxider af denne forbindelse;
og bestanddel (B) er en forbindelse valgt fra gruppen, der består af
(B1) et strobilurinfungicid,
(B2) et azolfungicid,
(B3) et anilinopyrimidinfungicid valgt fra gruppen, der består af cyprodinil, mepanipyrim og pyrimethanil;
(B4) fungicidet fluazinam,
(B5) isopyrazam og forbindelsen med formel (VII)



(VII).

2. Fungicidsammensætning, der omfatter en kombination af bestanddel (A) og (B) ifølge krav 1 i en synergistisk effektiv mængde.

3. Fremgangsmåde til beskyttelse af naturlige stoffer af plante- og/eller dyreoprindelse, der kan være taget fra den naturlige livscyklus, og/eller forarbejdede former deraf, hvor de naturlige stoffer af planteoprindelse er valgt fra gruppen, der består af planter eller dele deraf, der er i frisk høstet form, og de naturlige stoffer af dyreoprindelse er valgt fra gruppen af materialer, der består af hud, skind, læder og pels,

hvilken fremgangsmåde omfatter påføring på de naturlige stoffer af plante- og/eller dyreoprindelse eller de forarbejdede former deraf af en kombination af bestanddel (A) og (B) ifølge krav 1 i en synergistisk effektiv mængde med det forbehold, at påføringen af kombinationen af bestanddel (A) og (B) ikke indebærer påføring på kroppen af et levende dyr.

4. Fremgangsmåde ifølge krav 3, hvor de naturlige stoffer af planteoprindelse er frugter.