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(71) Applicant (for all designated States except US): **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JAMET, Laurent** [DE/FR]; 206 Route de Saint-Cyr, F-69009 Lyon (FR).

GERHARD, Ralf Willi [DE/DE]; Im Fronhof 4, 55278 Dexheim (DE).

(74) Common Representative: **BASF SE**; 67056 Ludwigshafen (DE).

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(54) Title: PESTICIDAL MIXTURES

(57) Abstract: The present invention relates to synergistic mixtures comprising, as active components, an insecticidal compound (I) selected from the nicotinic receptor agonists/antagonists compounds and one or two further fungicidal compounds in synergistic effective amounts.



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Pesticidal mixtures

Description

5 The present invention relates to synergistic mixtures comprising, as active components,

- 1) an insecticidal compound I selected from following nicotinic receptor agonists/antagonists compounds: acetamiprid, clothianidin, dinotefuran, imidacloprid, thiamethoxam, nitenpyram; and
- 10 2) one fungicidal compound(s) II selected from the group consisting of the azoles triticonazole, fluquinconazole, prothioconazole, difenoconazole, ipconazole, flutriafol and tebuconazole;
- 15 3) one or two further fungicidal compound(s) III selected from the group consisting of thiophanate-methyl, prochloraz, pyraclostrobin, azoxystrobin, trifloxystrobin, orysastrobin, metalaxyl, dimethomorph, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-[2-(4'-trifluoromethylthio)-biphenyl]-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazole-4-carboxamide (common name bixafen), N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (sedaxane), N-[1,2,3,4-tetrahydro-9-(1-methylethyl)-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (common name: isopyrazam) and N-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxamide (common name: penthiopyrad);
- 20 in synergistic effective amounts.

30 The invention furthermore relates to binary mixtures comprising comprising, as active components, acetamiprid and triticonazole.

The above-referred mixtures are hereinbelow also referred as "inventive mixtures".

35 Moreover, the invention relates to a method for controlling pests, this refers to includes animal pests and harmful fungi, using the inventive mixtures and to the use of compound I and the compound II and compound(s) III (or compound I and II as defined

above) for preparing such mixtures, and also to compositions comprising such mixtures.

5 In one embodiment, the present invention provides methods for the control of animal pests (such as insects, acarids or nematodes) comprising contacting the animal pest (the insect, acarid or nematode) or their food supply, habitat, breeding grounds or their locus with a pesticidally effective amount of the inventive mixtures.

10 Moreover, in another embodiment the present invention also relates to a method of protecting plants from attack or infestation by animal pests (insects, acarids or nematodes) comprising contacting the plant, or the soil or water in which the plant is growing, with a pesticidally effective amount of the inventive mixture.

15 Additionally, the present invention also comprises a method for protection of plant propagation material from harmful pests, such as fungi or insects, arachnids or nematodes comprising contacting the plant propagation material with an inventive mixture in pesticidally effective amounts

20 The term "plant propagation material" is to be understood to denote all the generative parts of the plant such as seeds and vegetative plant material such as cuttings and tubers (e. g. potatoes), which can be used for the multiplication of the plant. This includes seeds, roots, fruits, tubers, bulbs, rhizomes, shoots, sprouts and other parts of plants, including seedlings and young plants, which are to be transplanted after germination or after emergence from soil. These young plants may also be protected before
25 transplantation by a total or partial treatment by immersion or pouring. In a particular preferred embodiment, the term propagation material denotes seeds.

Moreover, the invention relates to a method for controlling harmful fungi using the inventive mixtures and to the use of the compound I and the compound II and compound(s) III (or compound I and II as defined above) for preparing such mixtures, and
30 also to compositions comprising such mixtures.

The present invention further relates to plant-protecting active ingredient mixtures having synergistically enhanced action of improving the health of plants and to a method of
35 applying such inventive mixtures to the plants.

The compounds of formula I, II and III as well as their pesticidal action and methods for producing them are generally known. For instance, the commercially available compounds may be found in The Pesticide Manual, 13th Edition, British Crop Protection
40 Council (2003) among other publications.

Herein, metalaxyl is a fungicide including: metalaxyl; metalaxyl consisting of equal or more than 50% by weight of the R-enantiomer and equal or less than 50% of the S-enantiomer; metalaxyl consisting of more than 85% by weight of the R-enantiomer less than 15% of the S-enantiomer; metalaxyl consisting of more than 92% by weight of the R-enantiomer and less than 8% of the S-enantiomer; metalaxyl consisting of more than 97% by weight of the R-enantiomer less than 3% of the S-enantiomer; and mefenoxam (i.e., more than 97.5% R-metalaxyl or metalaxyl-M and less than 2.5% of the S-enantiomer). See, for example, the Pesticide Manual, 11th Ed. (1997), The British Crop Protection Council, London, page 792; and the Pesticide Manual, 11th Ed. (1997), The British Crop Protection Council, London, page 794.

Binary mixtures comprising clothianidin together with a large listing of potential fungicidal mixing partners are disclosed in WO 99/63826.

Combinations generically comprising thiamethoxam and explicitly disclosing imidacloprid together with a large listing of potential fungicidal mixing partners are disclosed in WO 96/3045.

Triticonazole and prochloraz mixtures are disclosed in EP 467972, EP 466612 and PCT/EP2007/063417. Triticonazole and pyrimethanil mixtures are disclosed in FR 2742310. Prochloraz and pyrimethanil mixtures are disclosed in DE 4318372.

WO 06/069654, WO06/089876 and WO 06/23899 disclose mixtures of neonicotinoids and strobilurins. WO 06/23899 also discloses mixtures of imidacloprid and other fungicides.

WO 08/006541 discloses penthiopyrad mixtures with fungicides, which optionally may comprise an insecticide.

WO 97/22254 discloses mixtures of thiamethoxam with azoles such as triticonazole, pyrimethanil and prochloraz. WO 08/095891 comprises the mixture of clothianidin and triticonazole. WO 06/128655 disclosed mixtures of neonicotinoids with several azoles as well as mixtures of a huge number of insecticides that can be combined with several fungicides. WO 06/24333 describes a neonicotinoid formulation, which may, as second component comprise at least one further fungicide.

Binary mixtures comprising a specified carboxamide, epoxiconazole or metconazole, which may comprise a further commercial pesticide. Suitable ternary mixing partners mentioned therein are glyphosate, sulphosate, gluphosinate, tefluthrin, terbufos, chlorpyrifos, chloroethoxyfos, tebupirimfos, phenoxycarb, diofenolan, pymetrozine, imazethapyr, imazamox, imazapyr, imazapic, imazaquin or dimethenamid-P, in particular glyphosate, sulphosate, gluphosinate or dimethenamid-P, fipronil, imidacloprid, ace-

tamiprid, nitenpyram, carbofuran, carbosulfan, benfuracarb, dinotefuran, thiacloprid, thiamethoxam, clothianidin, diflubenzuron, flufenoxuron, teflubenzuron, alpha-cypermethrin and metaflumizone, in particular fipronil, imidacloprid, acetamiprid, carbofuran, thiamethoxam, clothianidin, flufenoxuron, teflubenzuron, alpha-cypermethrin and metaflumizone (EP application No. 08152059.5, EP application No. 08155881.9, EP application No. 07119858.4 and PCT/EP2008/051955).

Combinations comprising a specific carboxamide and orysastrobin and combinations amide of formula I, a strobilurine and thiophanate-methyl are disclosed in WO 07/017416. Combinations comprising amide compound of formula I and thiophanate-methyl are disclosed in PCT/EP2008/051331 and in PCT/EP2008/051375.

Combinations of specific amides of carboxamide together with neonicotinoids and fungicides are disclosed in WO 08/000377.

General disclosure about an amide of carboxamide together with a large fungicides or several insecticides are set forth in WO 07/128756.

However, the specific binary, ternary and quarternary mixtures of the present invention, which are based on a compound I and compound II and compound(s) III (or compound I and II as defined above) are not disclosed therein. In addition, the specific combinations of compound I and II as defined above, is also not mentioned therein.

One typical problem arising in the field of pest control lies in the need to reduce the dosage rates of the active ingredient in order to reduce or avoid unfavorable environmental or toxicological effects whilst still allowing effective pest control.

In regard to the instant invention the term pests embrace animal pests, and harmful fungi.

Another problem encountered concerns the need to have available pest control agents which are effective against a broad spectrum of pests, e.g. both animal pests and harmful fungi.

There also exists the need for pest control agents that combine knock-down activity with prolonged control, that is, fast action with long lasting action.

Another difficulty in relation to the use of pesticides is that the repeated and exclusive application of an individual pesticidal compound leads in many cases to a rapid selection of pests, that means animal pests, and harmful fungi, which have developed natural or adapted resistance against the active compound in question. Therefore there is a need for pest control agents that help prevent or overcome resistance.

Another problem underlying the present invention is the desire for compositions that improve plants, a process which is commonly and hereinafter referred to as "plant health".

5

The term plant health comprises various sorts of improvements of plants that are not connected to the control of pests. For example, advantageous properties that may be mentioned are improved crop characteristics including: emergence, crop yields, protein content, oil content, starch content, more developed root system (improved root growth), improved stress tolerance (e.g. against drought, heat, salt, UV, water, cold), reduced ethylene (reduced production and/or inhibition of reception), tillering increase, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf color, pigment content, photosynthetic activity, less input needed (such as fertilizers or water), less seeds needed, more productive tillers, earlier flowering, early grain maturity, less plant verse (lodging), increased shoot growth, enhanced plant vigor, increased plant stand and early and better germination; or any other advantages familiar to a person skilled in the art.

It was therefore an object of the present invention to provide pesticidal mixtures which solve the problems of reducing the dosage rate and / or enhancing the spectrum of activity and / or combining knock-down activity with prolonged control and / or to resistance management and/or promoting the health of plants.

We have found that this object is in part or in whole achieved by the complex mixtures comprising the active compounds defined in the outset.

Especially, it has been found that the mixtures as defined in the outset show markedly enhanced action against pests compared to the control rates that are possible with the individual compounds and/or is suitable for improving the health of plants when applied to plants, parts of plants, seeds, or at their locus of growth.

It has been found that the action of the inventive mixtures goes far beyond the fungicidal and/or insecticidal and/or plant health improving action of the active compounds present in the mixture alone.

35

Moreover, we have found that simultaneous, that is joint or separate, application of the compound I and the compound II and compound(s) III (or compound I and II as defined above) or successive application of the compound I and the compound II and compound(s) III (or compound I and II as defined above) allows enhanced control of pests, that means animal pests, and harmful fungi, compared to the control rates that are possible with the individual compounds (synergistic mixtures).

40

Preferably, the ternary or quaternary mixtures according to the present invention comprise as compound I clothianidin, imidacloprid, thiamethoxam or acetamiprid, more preferably clothianidin, imidacloprid or thiamethoxam.

- 5 Preferred compound II is triticonazole, prothiconazole, more preferably triticonazole.

- Preferred compounds III are those selected from the group consisting of thiophanate-methyl, prochloraz, pyraclostrobin, orysastrobin, metalaxyl, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (common name: sedaxane) and N-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxamide (common name: penthiopyrad), more preferred prochloraz, pyraclostrobin, orysastrobin, metalaxyl and N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, most preferred prochloraz, pyraclostrobin, metalaxyl and N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide.
- 10
15

- Preferred are the inventive ternary mixtures containing thiamethoxam as compound I.
- 20 Preferred are the inventive quaternary mixtures containing thiamethoxam as compound I.

- Preferred are the inventive ternary mixtures containing imidacloprid as compound I.
- Preferred are the inventive quaternary mixtures containing imidacloprid as compound I.
- 25

- Preferred are the inventive ternary mixtures containing clothianidin as compound I.
- Preferred are the inventive quaternary mixtures containing clothianidin as compound I.

- Preferred are the inventive ternary mixtures containing triticonazole as compound II.
- 30 Preferred are the inventive quaternary mixtures containing triticonazole as compound II.

- Preferred are the inventive ternary mixtures containing prochloraz as compound III.
- Preferred are the inventive quaternary mixtures containing prochloraz as compound III.
- 35

- Preferred are the inventive ternary mixtures containing pyraclostrobin as compound III.
- Preferred are the inventive quaternary mixtures containing pyraclostrobin as compound III.

- Preferred are the inventive ternary mixtures containing orysastrobin as compound III.
- Preferred are the inventive quaternary mixtures containing orysastrobin as compound III.
- 40

Preferred are the inventive ternary mixtures containing trifloxystrobin as compound III.
Preferred are the inventive quaternary mixtures containing trifloxystrobin as compound III.

5

Preferred are the inventive ternary mixtures containing azoxystrobin as compound III.
Preferred are the inventive quaternary mixtures containing azoxystrobin as compound III.

- 10 Preferred are the inventive ternary mixtures containing metalaxyl as compound III.
Preferred are the inventive quaternary mixtures containing metalaxyl as compound III.

Preferred are the inventive ternary mixtures containing N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide as compound III.

- 15 Preferred are the inventive quaternary mixtures containing N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide as compound III.

Preferred are the inventive ternary mixtures containing N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide as compound III.

- 20 Preferred are the inventive quaternary mixtures containing N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide as compound III.

Preferred are the inventive ternary mixtures containing N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide as compound III.

- 25 Preferred are the inventive quaternary mixtures containing N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (sedaxane), as compound III.

Preferred are the inventive ternary mixtures containing penthiopyrad as compound III.

- 30 Preferred are the inventive quaternary mixtures containing penthiopyrad as compound III.

The ratios by weight for the respective ternary mixtures comprising nicotinic receptor agonists/antagonists compound I, fungicidal compound II and one further fungicide III are from 1:100:100 to 100:1:1, preferably from 50:1:1 to 1:50:50, more preferably from 1:20:20 to 20:1:1.

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The ratios by weight for the respective quaternary mixtures comprising nicotinic receptor agonists/antagonists compound I, fungicidal compound II and two further fungicides III are from 1:100:100:100 to 100:1:1:1, preferably from 50:1:1:1 to 1:50:50:50, more preferably from 1:20:20:20 to 20:1:1:1.

40

The ratios by weight for the binary mixtures comprising as active components acetamiprid and triticonazole are from 1:100 to 100:1, preferably from 50:1 to 1:50, more preferably from 1:20 to 20.

5

With respect to their intended use, the following ternary and quaternary and mixtures of compound I (wherein compound I is clothianidin, imidacloprid or thiamethoxam) , compound II (which is triticonazole), one or two compound III (wherein compound III is selected from prothioconazole, prochloraz, metalaxyl, pyraclostrobin, orysastrobin, trifloxystrobin, thiophanate-methyl, azoxystrobin, compound Ia, Id, le or Ig) listed in the table 1 below are more preferred.

10

In addition to the abbreviations of table 1, the following abbreviations are used herein:

I is compound I

T = Trifloxystrobin

II is compound II

TPM = thiophanate-methyl

III (1) = 1st compound III

A = Azoxystrobin

III (2) = second compound III

TMX is thiamethoxam

Ia = N-(3',4',5'-trifluorobiphenyl-2-yl)- 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide,

I is imidacloprid

C is clothianidin

PC = Prothioconazole

Id = N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide,

TTZ = Triticonazole

Pz = Prochloraz

M= Metalaxyl

le =N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (sedaxane),

P = Pyraclostrobin

O = Orysastrobin.

Ig = penthiopyrad

15

Table 1

No	I	II	III (1)	III (2)
R-1	C	TTZ	Pz	
R-2	C	TTZ	Pz	M
R-3	C	TTZ	Pz	P
R-4	C	TTZ	Pz	O
R-5	C	TTZ	Pz	T
R-6	C	TTZ	Pz	A
R-7	C	TTZ	Pz	Ia
R-8	C	TTZ	Pz	Id
R-9	C	TTZ	Pz	le
R-10	C	TTZ	Pz	Ig

No	I	II	III (1)	III (2)
R-11	C	TTZ	Pz	TPM
R-12	C	TTZ	M	-
R-13	C	TTZ	M	P
R-14	C	TTZ	M	O
R-15	C	TTZ	M	T
R-16	C	TTZ	M	A
R-17	C	TTZ	M	la
R-18	C	TTZ	M	ld
R-19	C	TTZ	M	le
R-20	C	TTZ	M	lg
R-21	C	TTZ	M	TPM
R-22	C	TTZ	P	-
R-23	C	TTZ	P	O
R-24	C	TTZ	P	T
R-25	C	TTZ	P	A
R-26	C	TTZ	P	la
R-27	C	TTZ	P	ld
R-28	C	TTZ	P	le
R-29	C	TTZ	P	lg
R-30	C	TTZ	P	TPM
R-31	C	TTZ	O	-
R-32	C	TTZ	O	T
R-33	C	TTZ	O	A
R-34	C	TTZ	O	la
R-35	C	TTZ	O	ld
R-36	C	TTZ	O	le
R-37	C	TTZ	O	lg
R-38	C	TTZ	Pz	TPM
R-39	C	TTZ	T	-
R-40	C	TTZ	T	A
R-41	C	TTZ	T	la
R-42	C	TTZ	T	ld
R-43	C	TTZ	T	le
R-44	C	TTZ	T	lg
R-45	C	TTZ	T	TPM
R-46	C	TTZ	A	-
R-47	C	TTZ	A	la
R-48	C	TTZ	A	ld
R-49	C	TTZ	A	le
R-50	C	TTZ	A	lg

No	I	II	III (1)	III (2)
R-51	C	TTZ	A	TPM
R-52	C	TTZ	A	TPM
R-53	C	TTZ	la	-
R-54	C	TTZ	la	ld
R-55	C	TTZ	la	le
R-56	C	TTZ	la	lg
R-57	C	TTZ	la	TPM
R-58	C	TTZ	ld	-
R-59	C	TTZ	ld	le
R-60	C	TTZ	ld	lg
R-61	C	TTZ	le	lg
R-62	C	TTZ	le	TPM
R-63	C	TTZ	lg	-
R-64	C	TTZ	lg	TPM
R-65	C	TTZ	TPM	-
R-66	TMX	TTZ	Pz	
R-67	TMX	TTZ	Pz	M
R-68	TMX	TTZ	Pz	P
R-69	TMX	TTZ	Pz	O
R-70	TMX	TTZ	Pz	T
R-71	TMX	TTZ	Pz	A
R-72	TMX	TTZ	Pz	la
R-73	TMX	TTZ	Pz	ld
R-74	TMX	TTZ	Pz	le
R-75	TMX	TTZ	Pz	lg
R-76	TMX	TTZ	Pz	TPM
R-77	TMX	TTZ	M	-
R-78	TMX	TTZ	M	P
R-79	TMX	TTZ	M	O
R-80	TMX	TTZ	M	T
R-81	TMX	TTZ	M	A
R-82	TMX	TTZ	M	la
R-83	TMX	TTZ	M	ld
R-84	TMX	TTZ	M	le
R-85	TMX	TTZ	M	lg
R-86	TMX	TTZ	M	TPM
R-87	TMX	TTZ	P	-
R-88	TMX	TTZ	P	O
R-89	TMX	TTZ	P	T
R-90	TMX	TTZ	P	A

No	I	II	III (1)	III (2)
R-91	TMX	TTZ	P	la
R-92	TMX	TTZ	P	ld
R-93	TMX	TTZ	P	le
R-94	TMX	TTZ	P	lg
R-95	TMX	TTZ	P	TPM
R-96	TMX	TTZ	O	-
R-97	TMX	TTZ	O	T
R-98	TMX	TTZ	O	A
R-99	TMX	TTZ	O	la
R-100	TMX	TTZ	O	ld
R-101	TMX	TTZ	O	le
R-102	TMX	TTZ	O	lg
R-103	TMX	TTZ	Pz	TPM
R-104	TMX	TTZ	T	-
R-105	TMX	TTZ	T	A
R-106	TMX	TTZ	T	la
R-107	TMX	TTZ	T	ld
R-108	TMX	TTZ	T	le
R-109	TMX	TTZ	T	lg
R-110	TMX	TTZ	T	TPM
R-111	TMX	TTZ	A	-
R-112	TMX	TTZ	A	la
R-113	TMX	TTZ	A	ld
R-114	TMX	TTZ	A	le
R-115	TMX	TTZ	A	lg
R-116	TMX	TTZ	A	TPM
R-117	TMX	TTZ	A	TPM
R-118	TMX	TTZ	la	-
R-119	TMX	TTZ	la	ld
R-120	TMX	TTZ	la	le
R-121	TMX	TTZ	la	lg
R-122	TMX	TTZ	la	TPM
R-123	TMX	TTZ	ld	-
R-124	TMX	TTZ	ld	le
R-125	TMX	TTZ	ld	lg
R-126	TMX	TTZ	le	lg
R-127	TMX	TTZ	le	TPM
R-128	TMX	TTZ	lg	-
R-129	TMX	TTZ	lg	TPM
R-130	TMX	TTZ	TPM	-

No	I	II	III (1)	III (2)
R-131	I	TTZ	Pz	
R-132	I	TTZ	Pz	M
R-133	I	TTZ	Pz	P
R-134	I	TTZ	Pz	O
R-135	I	TTZ	Pz	T
R-136	I	TTZ	Pz	A
R-137	I	TTZ	Pz	Ia
R-138	I	TTZ	Pz	Id
R-139	I	TTZ	Pz	Ie
R-140	I	TTZ	Pz	Ig
R-141	I	TTZ	Pz	TPM
R-142	I	TTZ	M	-
R-143	I	TTZ	M	P
R-144	I	TTZ	M	O
R-145	I	TTZ	M	T
R-146	I	TTZ	M	A
R-147	I	TTZ	M	Ia
R-148	I	TTZ	M	Id
R-149	I	TTZ	M	Ie
R-150	I	TTZ	M	Ig
R-151	I	TTZ	M	TPM
R-152	I	TTZ	P	-
R-153	I	TTZ	P	O
R-154	I	TTZ	P	T
R-155	I	TTZ	P	A
R-156	I	TTZ	P	Ia
R-157	I	TTZ	P	Id
R-158	I	TTZ	P	Ie
R-159	I	TTZ	P	Ig
R-160	I	TTZ	P	TPM
R-161	I	TTZ	O	-
R-162	I	TTZ	O	T
R-163	I	TTZ	O	A
R-164	I	TTZ	O	Ia
R-165	I	TTZ	O	Id
R-166	I	TTZ	O	Ie
R-167	I	TTZ	O	Ig
R-168	I	TTZ	Pz	TPM
R-169	I	TTZ	T	-
R-170	I	TTZ	T	A

No	I	II	III (1)	III (2)
R-171	I	TTZ	T	Ia
R-172	I	TTZ	T	Id
R-173	I	TTZ	T	Ie
R-174	I	TTZ	T	Ig
R-175	I	TTZ	T	TPM
R-176	I	TTZ	A	-
R-177	I	TTZ	A	Ia
R-178	I	TTZ	A	Id
R-179	I	TTZ	A	Ie
R-180	I	TTZ	A	Ig
R-181	I	TTZ	A	TPM
R-182	I	TTZ	A	TPM
R-183	I	TTZ	Ia	-
R-184	I	TTZ	Ia	Id
R-185	I	TTZ	Ia	Ie
R-186	I	TTZ	Ia	Ig
R-187	I	TTZ	Ia	TPM
R-188	I	TTZ	Id	-
R-189	I	TTZ	Id	Ie
R-190	I	TTZ	Id	Ig
R-191	I	TTZ	Ie	Ig
R-192	I	TTZ	Ie	TPM
R-193	I	TTZ	Ig	-
R-194	I	TTZ	Ig	TPM
R-195	I	TTZ	TPM	-

Within these mixtures, the following mixtures are especially preferred:

R-1, R-3, R-13, R-12, R-22, R-26, R-27, R-28, R-29, R-30, R-65, R-66, R-68, R-78, R-77, R-87, R-91, R-92, R-93, R-94, R-95, R-130, R-131, R-133, R-143, R-142, R-152, R-156, R-157, R-158, R-159, R-160 and R-195.

Within this subset, the following mixtures are preferred: R-1, R-3, R-13, R-12, R-22, R-26, R-27, R-28, R-29, R-30, R-65, R-66, R-68, R-78, R-77, R-87, R-91, R-92, R-93, R-94, R-95, R-130, R-131, R-133, R-143, R-142, R-152, R-156, R-157, R-158, R-159, R-160 and R-195.

The inventive mixtures can further contain one or more insecticides, fungicides, herbicides.

For use according to the present invention, the mixtures according to the invention can be converted into the customary formulations, for example solutions, emulsions, sus-

pensions, dusts, powders, pastes and granules. The use form depends on the particular intended purpose; in each case, it should ensure a fine and even distribution of the mixtures according to the present invention. The formulations are prepared in a known manner (cf. US 3,060,084, EP-A 707 445 (for liquid concentrates), Browning: "Agglomeration", Chemical Engineering, Dec. 4, 1967, 147-48, Perry's Chemical Engineer's Handbook, 4th Ed., McGraw-Hill, New York, 1963, S. 8-57 und ff. WO 91/13546, US 4,172,714, US 4,144,050, US 3,920,442, US 5,180,587, US 5,232,701, US 5,208,030, GB 2,095,558, US 3,299,566, Klingman: Weed Control as a Science (J. Wiley & Sons, New York, 1961), Hance et al.: Weed Control Handbook (8th Ed., Blackwell Scientific, Oxford, 1989) and Mollet, H. and Grubemann, A.: Formulation technology (Wiley VCH Verlag, Weinheim, 2001).

The agrochemical formulations may also comprise auxiliaries which are customary in agrochemical formulations. The auxiliaries used depend on the particular application form and active substance, respectively.

Examples for suitable auxiliaries are solvents, solid carriers, dispersants or emulsifiers (such as further solubilizers, protective colloids, surfactants and adhesion agents), organic and anorganic thickeners, bactericides, anti-freezing agents, anti-foaming agents, if appropriate colorants and tackifiers or binders (e. g. for seed treatment formulations).

Suitable solvents are water, organic solvents such as mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e. g. toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, alcohols such as methanol, ethanol, propanol, butanol and cyclohexanol, glycols, ketones such as cyclohexanone and gamma-butyrolactone, fatty acid dimethylamides, fatty acids and fatty acid esters and strongly polar solvents, e. g. amines such as N-methylpyrrolidone.

Solid carriers are mineral earths such as silicates, silica gels, talc, kaolins, limestone, lime, chalk, bole, loess, clays, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, e. g., 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 and other solid carriers.

Suitable surfactants (adjuvants, wetters, tackifiers, dispersants or emulsifiers) are alkali metal, alkaline earth metal and ammonium salts of aromatic sulfonic acids, such as ligninsulfonic acid (Borresperse® types, Borregard, Norway) phenolsulfonic acid, naphthalenesulfonic acid (Morwet® types, Akzo Nobel, U.S.A.), dibutyl naphthalene-sulfonic acid (Nekal® types, BASF, Germany), and fatty acids, alkylsulfonates, alkyl-arylsulfonates, alkyl sulfates, lauryl ether sulfates, fatty alcohol sulfates, and sulfated hexa-, hepta- and octadecanates, sulfated fatty alcohol glycol ethers, furthermore condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxy-ethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol,

- nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite
- 5 waste liquors and proteins, denatured proteins, polysaccharides (e. g. methylcellulose), hydrophobically modified starches, polyvinyl alcohols (Mowiol® types, Clariant, Switzerland), polycarboxylates (Sokolan® types, BASF, Germany), polyalkoxylates, polyvinylamines (Lupasol® types, BASF, Germany), polyvinylpyrrolidone and the copolymers thereof.
- 10 Examples for thickeners (i. e. compounds that impart a modified flowability to formulations, i. e. high viscosity under static conditions and low viscosity during agitation) are polysaccharides and organic and anorganic clays such as Xanthan gum (Kelzan®, CP Kelco, U.S.A.), Rhodopol® 23 (Rhodia, France), Veegum® (R.T. Vanderbilt, U.S.A.) or Attaclay® (Engelhard Corp., NJ, USA).
- 15 Bactericides may be added for preservation and stabilization of the formulation. Examples for suitable bactericides are those based on dichlorophene and benzylalcohol hemi formal (Proxel® from ICI or Acticide® RS from Thor Chemie and Kathon® MK from Rohm & Haas) and isothiazolinone derivatives such as alkylisothiazolinones and benzisothiazolinones (Acticide® MBS from Thor Chemie).
- 20 Examples for suitable anti-freezing agents are ethylene glycol, propylene glycol, urea and glycerin.
- Examples for anti-foaming agents are silicone emulsions (such as e. g. Silikon® SRE, Wacker, Germany or Rhodorsil®, Rhodia, France), long chain alcohols, fatty acids, salts of fatty acids, fluoroorganic compounds and mixtures thereof.
- 25 Suitable colorants are pigments of low water solubility and water-soluble dyes. Examples to be mentioned und the designations rhodamin B, C. I. pigment red 112, C. I. solvent red 1, pigment blue 15:4, pigment blue 15:3, pigment blue 15:2, pigment blue 15:1, pigment blue 80, pigment yellow 1, pigment yellow 13, pigment red 112, pigment red 48:2, pigment red 48:1, pigment red 57:1, pigment red 53:1, pigment orange 43,
- 30 pigment orange 34, pigment orange 5, pigment green 36, pigment green 7, pigment white 6, pigment brown 25, basic violet 10, basic violet 49, acid red 51, acid red 52, acid red 14, acid blue 9, acid yellow 23, basic red 10, basic red 108.
- Examples for tackifiers or binders are polyvinylpyrrolidons, polyvinylacetates, polyvinyl alcohols and cellulose ethers (Tylose®, Shin-Etsu, Japan).
- 35 Powders, materials for spreading and dusts can be prepared by mixing or concomitantly grinding the compounds I and/or II and, if appropriate, further active substances, with at least one solid carrier.
- Granules, e. g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active substances to solid carriers. Examples of solid
- 40 carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, e. g.,

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 and other solid carriers.

5 Examples for formulation types are:

1. Composition types for dilution with water

i) Water-soluble concentrates (SL, LS)

10 10 parts by weight of compounds of the inventive mixtures are dissolved in 90 parts by weight of water or in a water-soluble solvent. As an alternative, wetting agents or other auxiliaries are added. The active substance dissolves upon dilution with water. In this way, a formulation having a content of 10% by weight of active substance is obtained.

ii) Dispersible concentrates (DC)

15 20 parts by weight of compounds of the inventive mixtures are dissolved in 70 parts by weight of cyclohexanone with addition of 10 parts by weight of a dispersant, e. g. polyvinylpyrrolidone. Dilution with water gives a dispersion. The active substance content is 20% by weight.

iii) Emulsifiable concentrates (EC)

20 15 parts by weight of compounds of the inventive mixtures are dissolved in 75 parts by weight of xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5 parts by weight). Dilution with water gives an emulsion. The composition has an active substance content of 15% by weight.

iv) Emulsions (EW, EO, ES)

25 25 parts by weight of compounds of the inventive mixtures are dissolved in 35 parts by weight of xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5 parts by weight). This mixture is introduced into 30 parts by weight of water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion. The composition has an active substance content of 25% by weight.

v) Suspensions (SC, OD, FS)

30 In an agitated ball mill, 20 parts by weight of compounds of the inventive mixtures are comminuted with addition of 10 parts by weight of dispersants and wetting agents and 70 parts by weight of water or an organic solvent to give a fine active substance suspension. Dilution with water gives a stable suspension of the active substance. The active substance content in the composition is 20% by weight.

35 vi) Water-dispersible granules and water-soluble granules (WG, SG)

40 50 parts by weight of compounds of the inventive mixtures are ground finely with addition of 50 parts by weight of dispersants and wetting agents and prepared as water-dispersible or water-soluble granules by means of technical appliances (e. g. extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active substance. The composition has an active substance content of 50% by weight.

vii) Water-dispersible powders and water-soluble powders (WP, SP, SS, WS)

75 parts by weight of compounds of the inventive mixtures are ground in a rotor-stator mill with addition of 25 parts by weight of dispersants, wetting agents and silica gel. Dilution with water gives a stable dispersion or solution of the active substance. The active substance content of the composition is 75% by weight.

5 viii) Gel (GF)

In an agitated ball mill, 20 parts by weight of compounds of the inventive mixtures are comminuted with addition of 10 parts by weight of dispersants, 1 part by weight of a gelling agent wetters and 70 parts by weight of water or of an organic solvent to give a fine suspension of the active substance. Dilution with water gives a stable suspension
10 of the active substance, whereby a composition with 20% (w/w) of active substance is obtained.

2. Composition types to be applied undiluted

ix) Dustable powders (DP, DS)

5 parts by weight of compounds of the inventive mixtures are ground finely and mixed
15 intimately with 95 parts by weight of finely divided kaolin. This gives a dustable composition having an active substance content of 5% by weight.

x) Granules (GR, FG, GG, MG)

0.5 parts by weight of compounds of the inventive mixtures is ground finely and associated with 99.5 parts by weight of carriers. Current methods are extrusion, spray-
20 drying or the fluidized bed. This gives granules to be applied undiluted having an active substance content of 0.5% by weight.

xi) ULV solutions (UL)

10 parts by weight of compounds of the inventive mixtures are dissolved in 90 parts by weight of an organic solvent, e. g. xylene. This gives a composition to be applied undi-
25 luted having an active substance content of 10% by weight.

The agrochemical formulations generally comprise between 0.01 and 95%, preferably between 0.1 and 90%, most preferably between 0.5 and 90%, by weight of active substances. The compounds of the inventive mixtures are employed in a purity of from
30 90% to 100%, preferably from 95% to 100% (according to NMR spectrum).

The compounds of the inventive mixtures can be used as such or in the form of their compositions, e. g. in the form of directly sprayable solutions, powders, suspensions, dispersions, emulsions, oil dispersions, pastes, dustable products, materials for
35 spreading, or granules, by means of spraying, atomizing, dusting, spreading, brushing, immersing or pouring. The application forms depend entirely on the intended purposes; it is intended to ensure in each case the finest possible distribution of the compounds present in the inventive mixtures.

40 Aqueous application forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or

solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

5

The active substance concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.001 to 1% by weight of compounds of the inventive mixtures .

10 The compounds of the inventive mixtures may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply compositions comprising over 95% by weight of active substance, or even to apply the active substance without additives.

15 Various types of oils, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, if appropriate not until immediately prior to use (tank mix). These agents can be admixed with the compounds of the inventive mixtures in a weight ratio of 1:100 to 100:1, preferably 1:10 to 10:1.

20 Compositions of this invention may also contain fertilizers such as ammonium nitrate, urea, potash, and superphosphate, phytotoxicants and plant growth regulators and safeners. These may be used sequentially or in combination with the above-described compositions, if appropriate also added only immediately prior to use (tank mix). For example, the plant(s) may be sprayed with a composition of this invention either before
25 or after being treated with the fertilizers.

The compounds contained in the mixtures as defined above can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

30

According to this invention, the compound I and II and compound (s) III (or compound I and II as defined above) is to be understood to denote, that at least the compound I and II and compound (s) III (or compound I and II as defined above) occur simultaneously at the site of action (i.e. the pests, such as harmful fungi and animal pests such
35 as insects, arachnids or nematods to be controlled or their habitats such as infected plants, plant propagation materials, particularly seeds, surfaces, materials or the soil as well as plants, plant propagation materials, particularly seeds, soil, surfaces, materials or rooms to be protected from fungal attack) in an effective amount.

40 This can be obtained by applying the compound I and II and compound (s) III (or compound I and II as defined above) simultaneously, either jointly (e. g. as tank-mix) or separately, or in succession, wherein the time interval between the individual applica-

tions is selected to ensure that the active substance applied first still occurs at the site of action in a sufficient amount at the time of application of the further active substance(s). The order of application is not essential for working of the present invention.

- 5 In binary, ternary and quaternary mixture of the present invention, the weight ratio of the compounds generally depends from the properties of the compounds of the inventive mixtures.

- 10 The compounds of the inventive mixtures can be used individually or already partially or completely mixed with one another to prepare the composition according to the invention. It is also possible for them to be packaged and used further as combination composition such as a kit of parts.

- 15 In one embodiment of the invention, the kits may include one or more, including all, components that may be used to prepare a subject agrochemical composition. E. g., kits may include the compound I and II and compound (s) III (or compound I and II as defined above) and/or an adjuvant component and/or a further pesticidal compound (e.g. insecticide or herbicide) and/or a growth regulator component). One or more of the components may already be combined together or pre-formulated. In those em-
20 bodiments where more than two components are provided in a kit, the components may already be combined together and as such are packaged in a single container such as a vial, bottle, can, pouch, bag or canister. In other embodiments, two or more components of a kit may be packaged separately, i. e., not pre-formulated. As such, kits may include one or more separate containers such as vials, cans, bottles, pouches,
25 bags or canisters, each container containing a separate component for an agrochemical composition. In both forms, a component of the kit may be applied separately from or together with the further components or as a component of a combination composition according to the invention for preparing the composition according to the invention.

- 30 The user applies the composition according to the invention usually from a predosage device, a knapsack sprayer, a spray tank or a spray plane. Here, the agrochemical composition is made up with water and/or buffer to the desired application concentration, it being possible, if appropriate, to add further auxiliaries, and the ready-to-use spray liquor or the agrochemical composition according to the invention is thus ob-
35 tained. Usually, 50 to 500 liters of the ready-to-use spray liquor are applied per hectare of agricultural useful area, preferably 100 to 400 liters.

- 40 According to one embodiment, individual compounds of the inventive mixtures formulated as composition (or formulation) such as parts of a kit or parts of a binary or ternary or quaternary mixture may be mixed by the user himself in a spray tank and further auxiliaries may be added, if appropriate (tank mix).

In a further embodiment, either individual compounds of the inventive mixtures formulated as composition or partially premixed components, e. g. components comprising the compound I and II and compound (s) III (or compound I and II as defined above) may be mixed by the user in a spray tank and further auxiliaries and additives may be added, if appropriate (tank mix).

In a further embodiment, either individual components of the composition according to the invention or partially premixed components, e. g. components comprising the compound I and II and compound (s) III (or compound I and II as defined above), can be applied jointly (e. .g. after tankmix) or consecutively.

As said above, the present invention comprises a method for controlling pests, that means animal pests and harmful fungi, wherein the pest, their habitat, breeding grounds, their locus or the plants to be protected against pest attack, the soil or plant propagation material (preferably seed) are treated with an pesticidally effective amount of a mixture.

Advantageously, the inventive mixtures are suitable for controlling the following fungal plant diseases:

Albugo spp. (white rust) on ornamentals, vegetables (e. g. *A. candida*) and sun-flowers (e. g. *A. tragopogonis*); *Alternaria* spp. (*Alternaria* leaf spot) on vegetables, rape (*A. brassicola* or *brassicae*), sugar beets (*A. tenuis*), fruits, rice, soybeans, potatoes (e. g. *A. solani* or *A. alternata*), tomatoes (e. g. *A. solani* or *A. alternata*) and wheat; *Aphanomyces* spp. on sugar beets and vegetables; *Ascochyta* spp. on cereals and vegetables, e. g. *A. tritici* (anthracnose) on wheat and *A. hordei* on barley; *Bipolaris* and *Drechslera* spp. (teleomorph: *Cochliobolus* spp.) on corn (e. g. *D. maydis*), cereals (e. g. *B. sorokiniana*: spot blotch), rice (e. g. *B. oryzae*) and turfs; *Blumeria* (formerly *Erysiphe*) *graminis* (powdery mildew) on cereals (e. g. on wheat or barley); *Botrytis cinerea* (teleomorph: *Botryotinia fuckeliana*: grey mold) on fruits and berries (e. g. strawberries), vegetables (e. g. lettuce, carrots, celery and cabbages), rape, flowers, vines, forestry plants and wheat; *Bremia lactucae* (downy mildew) on lettuce; *Ceratomyces* (syn. *Ophiostoma*) spp. (rot or wilt) on broad-leaved trees and evergreens, e. g. *C. ulmi* (Dutch elm disease) on elms; *Cercospora* spp. (*Cercospora* leaf spots) on corn, rice, sugar beets (e. g. *C. beticola*), sugar cane, vegetables, coffee, soybeans (e. g. *C. sojae* or *C. kikuchii*) and rice; *Cladosporium* spp. on tomatoes (e. g. *C. fulvum*: leaf mold) and cereals, e. g. *C. herbarum* (black ear) on wheat; *Claviceps purpurea* (ergot) on cereals; *Cochliobolus* (anamorph: *Helminthosporium* of *Bipolaris*) spp. (leaf spots) on corn (*C. carbonum*), cereals (e. g. *C. sativus*, anamorph: *B. sorokiniana*) and rice (e. g. *C. miyabeanus*, anamorph: *H. oryzae*); *Colletotrichum* (teleomorph: *Glomerella*) spp. (anthracnose) on cotton (e. g. *C. gossypii*), corn (e. g. *C. graminicola*), soft fruits, potatoes (e. g. *C. coccodes*: black dot), beans (e. g. *C. lindemuthianum*) and soybeans (e. g. *C. truncatum* or *C. gloeosporioides*); *Corticium* spp., e. g. *C. sasakii* (sheath

blight) on rice; *Corynespora cassiicola* (leaf spots) on soybeans and ornamentals;
Cycloconium spp., e. g. *C. oleaginum* on olive trees; *Cylindrocarpon* spp. (e. g. fruit
 tree canker or young vine decline, teleomorph: *Nectria* or *Neonectria* spp.) on fruit
 trees, vines (e. g. *C. liriodendri*, teleomorph: *Neonectria liriodendri*: Black Foot Disease)
 5 and ornamentals; *Dematophora* (teleomorph: *Rosellinia*) *necatrix* (root and stem rot) on
 soybeans; *Diaporthe* spp., e. g. *D. phaseolorum* (damping off) on soybeans; *Drechs-*
lera (syn. *Helminthosporium*, teleomorph: *Pyrenophora*) spp. on corn, cereals, such as
 barley (e. g. *D. teres*, net blotch) and wheat (e. g. *D. tritici-repentis*: tan spot), rice and
 turf; *Esca* (dieback, apoplexy) on vines, caused by *Formitiporia* (syn. *Phellinus*) *punc-*
 10 *tata*, *F. mediterranea*, *Phaeomoniella chlamydospora* (earlier *Phaeoacremonium chla-*
mydosporum), *Phaeoacremonium aleophilum* and/or *Botryosphaeria obtusa*; *Elsinoe*
 spp. on pome fruits (*E. pyri*), soft fruits (*E. veneta*: anthracnose) and vines (*E. ampe-*
lina: anthracnose); *Entyloma oryzae* (leaf smut) on rice; *Epicoccum* spp. (black mold)
 on wheat; *Erysiphe* spp. (powdery mildew) on sugar beets (*E. betae*), vegetables (e. g.
 15 *E. pisi*), such as cucurbits (e. g. *E. cichoracearum*), cabbages, rape (e. g. *E. crucife-*
rarum); *Eutypa lata* (*Eutypa* canker or dieback, anamorph: *Cytosporina lata*, syn. *Liber-*
tella blepharis) on fruit trees, vines and ornamental woods; *Exserohilum* (syn. *Helmin-*
thosporium) spp. on corn (e. g. *E. turcicum*); *Fusarium* (teleomorph: *Gibberella*) spp.
 (wilt, root or stem rot) on various plants, such as *F. graminearum* or *F. culmorum* (root
 20 rot, scab or head blight) on cereals (e. g. wheat or barley), *F. oxysporum* on tomatoes,
F. solani on soybeans and *F. verticillioides* on corn; *Gaeumannomyces graminis* (take-
 all) on cereals (e. g. wheat or barley) and corn; *Gibberella* spp. on cereals (e. g. *G.*
zeae) and rice (e. g. *G. fujikuroi*: Bakanae disease); *Glomerella cingulata* on vines,
 pome fruits and other plants and *G. gossypii* on cotton; Grainstaining complex on rice;
 25 *Guignardia bidwellii* (black rot) on vines; *Gymnosporangium* spp. on rosaceous plants
 and junipers, e. g. *G. sabinae* (rust) on pears; *Helminthosporium* spp. (syn. *Drechslera*,
 teleomorph: *Cochliobolus*) on corn, cereals and rice; *Hemileia* spp., e. g. *H. vastatrix*
 (coffee leaf rust) on coffee; *Isariopsis clavispora* (syn. *Cladosporium vitis*) on vines;
Macrophomina phaseolina (syn. *phaseoli*) (root and stem rot) on soybeans and cotton;
 30 *Microdochium* (syn. *Fusarium*) *nivale* (pink snow mold) on cereals (e. g. wheat or bar-
 ley); *Microsphaera diffusa* (powdery mildew) on soybeans; *Monilinia* spp., e. g. *M. laxa*,
M. fructicola and *M. fructigena* (bloom and twig blight, brown rot) on stone fruits and
 other rosaceous plants; *Mycosphaerella* spp. on cereals, bananas, soft fruits and
 ground nuts, such as e. g. *M. graminicola* (anamorph: *Septoria tritici*, *Septoria blotch*)
 35 on wheat or *M. fijiensis* (black Sigatoka disease) on bananas; *Peronospora* spp.
 (downy mildew) on cabbage (e. g. *P. brassicae*), rape (e. g. *P. parasitica*), onions (e. g.
P. destructor), tobacco (*P. tabacina*) and soybeans (e. g. *P. manshurica*); *Phakopsora*
pachyrhizi and *P. meibomiae* (soybean rust) on soybeans; *Phialophora* spp. e. g. on
 vines (e. g. *P. tracheiphila* and *P. tetraspora*) and soybeans (e. g. *P. gregata*: stem rot);
 40 *Phoma lingam* (root and stem rot) on rape and cabbage and *P. betae* (root rot, leaf
 spot and damping-off) on sugar beets; *Phomopsis* spp. on sunflowers, vines (e. g. *P.*
viticola: can and leaf spot) and soybeans (e. g. stem rot: *P. phaseoli*, teleomorph: *Di-*

aporthae phaseolorum); *Physoderma maydis* (brown spots) on corn; *Phytophthora* spp. (wilt, root, leaf, fruit and stem rot) on various plants, such as paprika and cucurbits (e. g. *P. capsici*), soybeans (e. g. *P. megasperma*, syn. *P. sojae*), potatoes and tomatoes (e. g. *P. infestans*: late blight) and broad-leaved trees (e. g. *P. ramorum*: sudden oak death); *Plasmodiophora brassicae* (club root) on cabbage, rape, radish and other plants; *Plasmopara* spp., e. g. *P. viticola* (grapevine downy mildew) on vines and *P. halstedii* on sunflowers; *Podosphaera* spp. (powdery mildew) on rosaceous plants, hop, pome and soft fruits, e. g. *P. leucotricha* on apples; *Polymyxa* spp., e. g. on cereals, such as barley and wheat (*P. graminis*) and sugar beets (*P. betae*) and thereby transmitted viral diseases; *Pseudocercospora herpotrichoides* (eyespot, teleomorph: *Tapesia yallundae*) on cereals, e. g. wheat or barley; *Pseudoperonospora* (downy mildew) on various plants, e. g. *P. cubensis* on cucurbits or *P. humili* on hop; *Pseudopeziza tracheiphila* (red fire disease or 'rotbrenner', anamorph: *Phialophora*) on vines; *Puccinia* spp. (rusts) on various plants, e. g. *P. tritici* (brown or leaf rust), *P. striiformis* (stripe or yellow rust), *P. hordei* (dwarf rust), *P. graminis* (stem or black rust) or *P. recondita* (brown or leaf rust) on cereals, such as e. g. wheat, barley or rye, and asparagus (e. g. *P. asparagi*); *Pyrenophora* (anamorph: *Drechslera*) *tritici-repentis* (tan spot) on wheat or *P. teres* (net blotch) on barley; *Pyricularia* spp., e. g. *P. oryzae* (teleomorph: *Magnaporthe grisea*, rice blast) on rice and *P. grisea* on turf and cereals; *Pythium* spp. (damping-off) on turf, rice, corn, wheat, cotton, rape, sunflowers, soybeans, sugar beets, vegetables and various other plants (e. g. *P. ultimum* or *P. aphanidermatum*); *Ramularia* spp., e. g. *R. collo-cygni* (*Ramularia* leaf spots, Physiological leaf spots) on barley and *R. beticola* on sugar beets; *Rhizoctonia* spp. on cotton, rice, potatoes, turf, corn, rape, potatoes, sugar beets, vegetables and various other plants, e. g. *R. solani* (root and stem rot) on soybeans, *R. solani* (sheath blight) on rice or *R. cerealis* (*Rhizoctonia* spring blight) on wheat or barley; *Rhizopus stolonifer* (black mold, soft rot) on strawberries, carrots, cabbage, vines and tomatoes; *Rhynchosporium secalis* (scald) on barley, rye and triticale; *Sarocladium oryzae* and *S. attenuatum* (sheath rot) on rice; *Sclerotinia* spp. (stem rot or white mold) on vegetables and field crops, such as rape, sunflowers (e. g. *S. sclerotiorum*) and soybeans (e. g. *S. rolfsii* or *S. sclerotiorum*); *Septoria* spp. on various plants, e. g. *S. glycines* (brown spot) on soybeans, *S. tritici* (*Septoria* blotch) on wheat and *S.* (syn. *Stagonospora*) *nodorum* (*Stagonospora* blotch) on cereals; *Uncinula* (syn. *Erysiphe*) *necator* (powdery mildew, anamorph: *Oidium tuckeri*) on vines; *Setosphaeria* spp. (leaf blight) on corn (e. g. *S. turcicum*, syn. *Helminthosporium turcicum*) and turf; *Sphacelotheca* spp. (smut) on corn, (e. g. *S. reiliana*: head smut), sorghum and sugar cane; *Sphaerotheca fuliginea* (powdery mildew) on cucurbits; *Spongospora subterranea* (powdery scab) on potatoes and thereby transmitted viral diseases; *Stagonospora* spp. on cereals, e. g. *S. nodorum* (*Stagonospora* blotch, teleomorph: *Leptosphaeria* [syn. *Phaeosphaeria*] *nodorum*) on wheat; *Synchytrium endobioticum* on potatoes (potato wart disease); *Taphrina* spp., e. g. *T. deformans* (leaf curl disease) on peaches and *T. pruni* (plum pocket) on plums; *Thielaviopsis* spp. (black root rot) on tobacco, pome fruits, vegetables, soybeans and

cotton, e. g. *T. basicola* (syn. *Chalara elegans*); *Tilletia* spp. (common bunt or stinking smut) on cereals, such as e. g. *T. tritici* (syn. *T. caries*, wheat bunt) and *T. controversa* (dwarf bunt) on wheat; *Typhula incarnata* (grey snow mold) on barley or wheat; *Urocystis* spp., e. g. *U. occulta* (stem smut) on rye; *Uromyces* spp. (rust) on vegetables, such as beans (e. g. *U. appendiculatus*, syn. *U. phaseoli*) and sugar beets (e. g. *U. betae*); *Ustilago* spp. (loose smut) on cereals (e. g. *U. nuda* and *U. avenae*), corn (e. g. *U. maydis*: corn smut) and sugar cane; *Venturia* spp. (scab) on apples (e. g. *V. inaequalis*) and pears; and *Verticillium* spp. (wilt) on various plants, such as fruits and ornamentals, vines, soft fruits, vegetables and field crops, e. g. *V. dahliae* on strawberries, rape, potatoes and tomatoes.

The inventive mixtures are also suitable for controlling harmful fungi in the protection of materials (e. g. wood, paper, paint dispersions, fiber or fabrics) and in the protection of stored products. As to the protection of wood and construction materials, the particular attention is paid to the following harmful fungi: Ascomycetes such as *Ophiostoma* spp., *Ceratocystis* spp., *Aureobasidium pullulans*, *Sclerophoma* spp., *Chaetomium* spp., *Humicola* spp., *Petriella* spp., *Trichurus* spp.; Basidiomycetes such as *Coniophora* spp., *Coriolus* spp., *Gloeophyllum* spp., *Lentinus* spp., *Pleurotus* spp., *Poria* spp., *Serpula* spp. and *Tyromyces* spp.; Deuteromycetes such as *Aspergillus* spp., *Cladosporium* spp., *Penicillium* spp., *Trichormia* spp., *Alternaria* spp., *Paecilomyces* spp. and Zygomycetes such as *Mucor* spp., and in addition in the protection of stored products the following yeast fungi are worthy of note: *Candida* spp. and *Saccharomyces cerevisiae*.

They are particularly important for controlling a multitude of fungi on various cultivated plants, such as bananas, cotton, vegetable species (for example cucumbers, beans and cucurbits), barley, grass, oats, coffee, potatoes, corn, fruit species, rice, rye, soya, tomatoes, grapevines, wheat, ornamental plants, sugar cane and also on a large number of plant propagation materials (preferably seeds).

The inventive mixtures exhibit also outstanding action against animal pests from the following orders:

insects from the order of the lepidopterans (Lepidoptera), for example *Agrotis ypsilon*, *Agrotis segetum*, *Alabama argillacea*, *Anticarsia gemmatilis*, *Argyresthia conjugella*, *Autographa gamma*, *Bupalus piniarius*, *Cacoecia murinana*, *Capua reticulana*, *Cheimatobia brumata*, *Choristoneura fumiferana*, *Choristoneura occidentalis*, *Cirphis unipuncta*, *Cydia pomonella*, *Dendrolimus pini*, *Diaphania nitidalis*, *Diatraea grandiosella*, *Earias insulana*, *Elasmopalpus lignosellus*, *Eupoecilia ambiguella*, *Evetria bouliana*, *Feltia subterranea*, *Galleria mellonella*, *Grapholitha funebrana*, *Grapholitha molesta*, *Heliothis armigera*, *Heliothis virescens*, *Heliothis zea*, *Hellula undalis*, *Hibernia defoliaria*, *Hyphantria cunea*, *Hyponomeuta malinellus*, *Keiferia lycopersicella*, *Lambdina fiscellaria*, *Laphygma exigua*, *Leucoptera coffeella*, *Leucoptera scitella*, *Lithocol-*

- letis blancardella, Lobesia botrana, Loxostege sticticalis, Lymantria dispar, Lymantria monacha, Lyonetia clerkella, Malacosoma neustria, Mamestra brassicae, Orgyia pseudotsugata, Ostrinia nubilalis, Panolis flammea, Pectinophora gossypiella, Peridroma saucia, Phalera bucephala, Phthorimaea operculella, Phyllocnistis citrella, Pieris brassicae, Plathypena scabra, Plutella xylostella, Pseudoplusia includens, Rhyacionia frugiperda, Scrobipalpula absoluta, Sitotroga cerealella, Sparganothis pilleriana, Spodoptera frugiperda, Spodoptera littoralis, Spodoptera litura, Thaumtopoea pityocampa, Tortrix viridana, Trichoplusia ni and Zeiraphera canadensis,
- 10 beetles (Coleoptera), for example Agrilus sinuatus, Agriotes lineatus, Agriotes obscurus, Amphimallus solstitialis, Anisandrus dispar, Anthonomus grandis, Anthonomus pomorum, Aphthona euphoridae, Athous haemorrhoidalis, Atomaria linearis, Blastophagus piniperda, Blitophaga undata, Bruchus rufimanus, Bruchus pisorum, Bruchus lentis, Byctiscus betulae, Cassida nebulosa, Cerotoma trifurcata, Cetonia aurata,
- 15 Ceuthorrhynchus assimilis, Ceuthorrhynchus napi, Chaetocnema tibialis, Conoderus vespertinus, Crioceris asparagi, Ctenicera ssp., Diabrotica longicornis, Diabrotica semipunctata, Diabrotica 12-punctata Diabrotica speciosa, Diabrotica virgifera, Epilachna varivestis, Epitrix hirtipennis, Eutinobothrus brasiliensis, Hylobius abietis, Hypera brunneipennis, Hypera postica, Ips typographus, Lema bilineata, Lema melanopus,
- 20 Leptinotarsa decemlineata, Limonius californicus, Lissorhoptrus oryzophilus, Melanotus communis, Meligethes aeneus, Melolontha hippocastani, Melolontha melolontha, Oulema oryzae, Ortiorrhynchus sulcatus, Otiorrhynchus ovatus, Phaedon cochleariae, Phyllobius pyri, Phyllotreta chrysocephala, Phyllophaga sp., Phyllopertha horticola, Phyllotreta nemorum, Phyllotreta striolata, Popillia japonica, Sitona lineatus and Sitophilus granaria,
- 25 flies, mosquitoes (Diptera), e.g. Aedes aegypti, Aedes albopictus, Aedes vexans, Anastrepha ludens, Anopheles maculipennis, Anopheles crucians, Anopheles albimanus, Anopheles gambiae, Anopheles freeborni, Anopheles leucosphyrus, Anopheles minimus, Anopheles quadrimaculatus, Calliphora vicina, Ceratitis capitata, Chrysomya bezziana, Chrysomya hominivorax, Chrysomya macellaria, Chrysops discalis, Chrysops silacea, Chrysops atlanticus, Cochliomyia hominivorax, Contarinia sorghicola Cordylobia anthropophaga, Culicoides furens, Culex pipiens, Culex nigripalpus, Culex quinquefasciatus, Culex tarsalis, Culiseta inornata, Culiseta melanura, Dacus cucurbitae, Dacus oleae, Dasineura brassicae, Delia antique, Delia coarctata, Delia platura, Delia radicum, Dermatobia hominis, Fannia canicularis, Geomyza tripunctata, Gasterophilus intestinalis, Glossina morsitans, Glossina palpalis, Glossina fuscipes, Glossina tachinoides, Haematobia irritans, Haplodiplosis equestris, Hippelates spp., Hylemyia platura, Hypoderma lineata, Leptoconops torrens, Liriomyza sativae, Liriomyza trifolii,
- 35 Lucilia caprina, Lucilia cuprina, Lucilia sericata, Lycoria pectoralis, Mansonia titillanus, Mayetiola destructor, Musca domestica, Muscina stabulans, Oestrus ovis, Opomyza florum, Oscinella frit, Pegomya hysocyami, Phorbia antiqua, Phorbia brassicae, Phor-
- 40

- bia coarctata, *Phlebotomus argentipes*, *Psorophora columbiae*, *Psila rosae*, *Psorophora discolor*, *Prosimulium mixtum*, *Rhagoletis cerasi*, *Rhagoletis pomonella*, *Sarcophaga haemorrhoidalis*, *Sarcophaga* sp., *Simulium vittatum*, *Stomoxys calcitrans*, *Tabanus bovinus*, *Tabanus atratus*, *Tabanus lineola*, and *Tabanus similis*, *Tipula ol-
eracea*, and *Tipula paludosa*
- thrips (Thysanoptera), e.g. *Dichromothrips corbetti*, *Dichromothrips* ssp , *Frankliniella fusca*, *Frankliniella occidentalis*, *Frankliniella tritici*, *Scirtothrips citri*, *Thrips oryzae*, *Thrips palmi* and *Thrips tabaci*,
- termites (Isoptera), e.g. *Calotermes flavicollis*, *Leucotermes flavipes*, *Heterotermes aureus*, *Reticulitermes flavipes*, *Reticulitermes virginicus*, *Reticulitermes lucifugus*, *Termes natalensis*, and *Coptotermes formosanus*,
- cockroaches (Blattaria - Blattodea), e.g. *Blattella germanica*, *Blattella asahinae*, *Periplaneta americana*, *Periplaneta japonica*, *Periplaneta brunnea*, *Periplaneta fuliginosa*, *Periplaneta australasiae*, and *Blatta orientalis*,
- true bugs (Hemiptera), e.g. *Acrosternum hilare*, *Blissus leucopterus*, *Cyrtopeltis notatus*, *Dysdercus cingulatus*, *Dysdercus intermedius*, *Eurygaster integriceps*, *Euschistus impictiventris*, *Leptoglossus phyllopus*, *Lygus lineolaris*, *Lygus pratensis*, *Nezara viridula*, *Piesma quadrata*, *Solubea insularis* , *Thyanta perditor*, *Acyrtosiphon onobrychis*, *Adelges laricis*, *Aphidula nasturtii*, *Aphis fabae*, *Aphis forbesi*, *Aphis pomi*, *Aphis gossypii*, *Aphis grossulariae*, *Aphis schneideri*, *Aphis spiraeicola*, *Aphis sambuci*, *Acyrtosiphon pisum*, *Aulacorthum solani*, *Bemisia argentifolii*, *Brachycaudus cardui*, *Brachycaudus helichrysi*, *Brachycaudus persicae*, *Brachycaudus prunicola*, *Brevicoryne brassicae*, *Capitophorus horni*, *Cerosipha gossypii*, *Chaetosiphon fragaefolii*, *Cryptomyzus ribis*, *Dreyfusia nordmannianae*, *Dreyfusia piceae*, *Dysaphis radicola*, *Dysaulacorthum pseudosolani*, *Dysaphis plantaginea*, *Dysaphis pyri*, *Empoasca fabae*, *Hyalopterus pruni*, *Hyperomyzus lactucae*, *Macrosiphum avenae*, *Macrosiphum euphorbiae*, *Macrosiphon rosae*, *Megoura viciae*, *Melanaphis pyraeius*, *Metopolophium dirhodum*, *Myzus persicae*, *Myzus ascalonicus*, *Myzus cerasi*, *Myzus varians*, *Nasonovia ribis-nigri*, *Nilaparvata lugens*, *Pemphigus bursarius*, *Perkinsiella saccharicida*, *Phorodon humuli*, *Psylla mali*, *Psylla piri*, *Rhopalomyzus ascalonicus*, *Rhopalosiphum maidis*, *Rhopalosiphum padi*, *Rhopalosiphum insertum*, *Sappaphis mala*, *Sappaphis mali*, *Schizaphis graminum*, *Schizoneura lanuginosa*, *Sitobion avenae*, *Trialeurodes vaporariorum*, *Toxoptera aurantiand*, *Viteus vitifolii*, *Cimex lectularius*, *Cimex hemipterus*, *Reduvius senilis*, *Triatoma* spp., and *Arilus critatus*.
- ants, bees, wasps, sawflies (Hymenoptera), e.g. *Athalia rosae*, *Atta cephalotes*, *Atta capiguara*, *Atta cephalotes*, *Atta laevigata*, *Atta robusta*, *Atta sexdens*, *Atta texana*, *Crematogaster* spp., *Hoplocampa minuta*, *Hoplocampa testudinea*, *Monomorium pha-*

- raonis, *Solenopsis geminata*, *Solenopsis invicta*, *Solenopsis richteri*, *Solenopsis xyloni*, *Pogonomyrmex barbatus*, *Pogonomyrmex californicus*, *Pheidole megacephala*, *Dasy-
mutilla occidentalis*, *Bombus* spp. *Vespula squamosa*, *Paravespula vulgaris*, *Paraves-
pula pennsylvanica*, *Paravespula germanica*, *Dolichovespula maculata*, *Vespa crabro*,
5 *Polistes rubiginosa*, *Camponotus floridanus*, and *Linepithema humile*,
- crickets, grasshoppers, locusts (Orthoptera), e.g. *Acheta domestica*, *Gryllotalpa gryllo-
talpa*, *Locusta migratoria*, *Melanoplus bivittatus*, *Melanoplus femurrubrum*, *Melanoplus
mexicanus*, *Melanoplus sanguinipes*, *Melanoplus spretus*, *Nomadacris septemfasciata*,
10 *Schistocerca americana*, *Schistocerca gregaria*, *Dociostaurus maroccanus*, *Tachycines
asynamorus*, *Oedaleus senegalensis*, *Zonozelus variegatus*, *Hieroglyphus daganensis*,
Kraussaria angulifera, *Calliptamus italicus*, *Chortoicetes terminifera*, and *Locustana
pardalina*,
- 15 Arachnoidea, such as arachnids (Acarina), e.g. of the families Argasidae, Ixodidae and
Sarcoptidae, such as *Amblyomma americanum*, *Amblyomma variegatum*, *Ambryomma
maculatum*, *Argas persicus*, *Boophilus annulatus*, *Boophilus decoloratus*, *Boophilus
microplus*, *Dermacentor silvarum*, *Dermacentor andersoni*, *Dermacentor variabilis*,
20 *Hyalomma truncatum*, *Ixodes ricinus*, *Ixodes rubicundus*, *Ixodes scapularis*, *Ixodes
holocyclus*, *Ixodes pacificus*, *Ornithodoros moubata*, *Ornithodoros hermsi*, *Orni-
thodoros turicata*, *Ornithonyssus bacoti*, *Otobius megnini*, *Dermanyssus gallinae*, *Pso-
roptes ovis*, *Rhipicephalus sanguineus*, *Rhipicephalus appendiculatus*, *Rhipicephalus
evertsi*, *Sarcoptes scabiei*, and Eriophyidae spp. such as *Aculus schlechtendali*, *Phyl-
locoptrata oleivora* and Eriophyes sheldoni; Tarsonemidae spp. such as *Phytonemus
25 pallidus* and *Polyphagotarsonemus latus*; Tenuipalpidae spp. such as *Brevipalpus
phoenicis*; Tetranychidae spp. such as *Tetranychus cinnabarinus*, *Tetranychus kan-
zawai*, *Tetranychus pacificus*, *Tetranychus telarius* and *Tetranychus urticae*, *Panony-
chus ulmi*, *Panonychus citri*, and *Oligonychus pratensis*; Araneida, e.g. *Latrodectus
30 mactans*, and *Loxosceles reclusa*,
- fleas (Siphonaptera), e.g. *Ctenocephalides felis*, *Ctenocephalides canis*, *Xenopsylla
cheopis*, *Pulex irritans*, *Tunga penetrans*, and *Nosopsyllus fasciatus*,
- silverfish, firebrat (Thysanura), e.g. *Lepisma saccharina* and *Thermobia domestica*,
35 centipedes (Chilopoda), e.g. *Scutigera coleoptrata*,
- millipedes (Diplopoda), e.g. *Narceus* spp.,
- 40 Earwigs (Dermaptera), e.g. *forficula auricularia*,

lice (Phthiraptera), e.g. *Pediculus humanus capitis*, *Pediculus humanus corporis*, *Phthirus pubis*, *Haematopinus eurysternus*, *Haematopinus suis*, *Linognathus vituli*, *Bovicola bovis*, *Menopon gallinae*, *Menacanthus stramineus* and *Solenopotes capillatus*,

- 5 plant parasitic nematodes such as root-knot nematodes, *Meloidogyne arenaria*, *Meloidogyne chitwoodi*, *Meloidogyne exigua*, *Meloidogyne hapla*, *Meloidogyne incognita*, *Meloidogyne javanica* and other *Meloidogyne* species; cyst nematodes, *Globodera rostochiensis*, *Globodera pallida*, *Globodera tabacum* and other *Globodera* species, *Heterodera avenae*, *Heterodera glycines*, *Heterodera schachtii*, *Heterodera trifolii*, and
- 10 other *Heterodera* species; seed gall nematodes, *Anguina funesta*, *Anguina tritici* and other *Anguina* species; stem and foliar nematodes, *Aphelenchoides besseyi*, *Aphelenchoides fragariae*, *Aphelenchoides ritzemabosi* and other *Aphelenchoides* species; sting nematodes, *Belonolaimus longicaudatus* and other *Belonolaimus* species; pine nematodes, *Bursaphelenchus xylophilus* and other *Bursaphelenchus* species; ring ne-
- 15 matodes, *Criconema* species, *Criconemella* species, *Criconemoides* species, and *Mesocriconema* species; stem and bulb nematodes, *Ditylenchus destructor*, *Ditylenchus dipsaci*, *Ditylenchus myceliophagus* and other *Ditylenchus* species; awl nematodes, *Dolichodorus* species; spiral nematodes, *Helicotylenchus dihystra*, *Helicotylenchus multicinctus* and other *Helicotylenchus* species, *Rotylenchus robustus* and other *Roty-*
- 20 *lenchus* species; sheath nematodes, *Hemicyclophora* species and *Hemicriconemoides* species; *Hirshmanniella* species; lance nematodes, *Hoplolaimus columbus*, *Hoplolaimus galeatus* and other *Hoplolaimus* species; false root-knot nematodes, *Nacobbus aberrans* and other *Nacobbus* species; needle nematodes, *Longidorus elongatus* and other *Longidorus* species; pin nematodes, *Pratylenchus* species; lesion nema-
- 25 todes, *Pratylenchus brachyurus*, *Pratylenchus coffeae*, *Pratylenchus curvatus*, *Pratylenchus goodeyi*, *Pratylenchus neglectus*, *Pratylenchus penetrans*, *Pratylenchus scribneri*, *Pratylenchus vulnus*, *Pratylenchus zeae* and other *Pratylenchus* species; *Radinaphelenchus cocophilus* and other *Radinaphelenchus* species; burrowing nema-
- 30 todes, *Radopholus similis* and other *Radopholus* species; reniform nematodes, *Rotylenchulus reniformis* and other *Rotylenchulus* species; *Scutellonema* species; stubby root nematodes, *Trichodorus primitivus* and other *Trichodorus* species; *Paratrichodorus minor* and other *Paratrichodorus* species; stunt nematodes, *Tylenchorhynchus claytoni*, *Tylenchorhynchus dubius* and other *Tylenchorhynchus* species and *Merlinius* species; citrus nematodes, *Tylenchulus semipenetrans* and other *Tylenchulus* species; dagger
- 35 nematodes, *Xiphinema americanum*, *Xiphinema index*, *Xiphinema diversicaudatum* and other *Xiphinema* species; and other plant parasitic nematode species.

The mixtures according to the invention can be applied to any and all developmental stages of pests, such as egg, larva, pupa, and adult. The pests may be controlled by

40 contacting the target pest, its food supply, habitat, breeding ground or its locus with a pesticidally effective amount of the inventive mixtures or of compositions comprising the mixtures.

"Locus" means a plant, plant propagation material (preferably seed), soil, area, material or environment in which a pest is growing or may grow.

5 In general, "pesticidally effective amount" means the amount of the inventive mixtures or of compositions comprising the mixtures needed to achieve an observable effect on growth, including the effects of necrosis, death, retardation, prevention, and removal, destruction, or otherwise diminishing the occurrence and activity of the target organism. The pesticidally effective amount can vary for the various mixtures / compositions used
10 in the invention. A pesticidally effective amount of the mixtures / compositions will also vary according to the prevailing conditions such as desired pesticidal effect and duration, weather, target species, locus, mode of application, and the like.

As said above, the present invention comprises a method for improving the health of
15 plants, wherein the plant, the locus where the plant is growing or is expected to grow or plant propagation material, from which the plant grows, is treated with an plant health effective amount of an inventive mixture.

The term "plant effective amount" denotes an amount of the inventive mixtures, which
20 is sufficient for achieving plant health effects as defined hereinbelow. More exemplary information about amounts, ways of application and suitable ratios to be used is given below. Anyway, the skilled artisan is well aware of the fact that such an amount can vary in a broad range and is dependent on various factors, e.g. the treated cultivated plant or material and the climatic conditions.

25 When preparing the mixtures, it is preferred to employ the pure active compounds, to which further active compounds against pests, such as insecticides, herbicides, fungicides or else herbicidal or growth-regulating active compounds or fertilizers can be added as further active components according to need.

30 The inventive mixtures are employed by treating the fungi or the plants, plant propagation materials (preferably seeds), materials or soil to be protected from fungal attack with a pesticidally effective amount of the active compounds. The application can be carried out both before and after the infection of the materials, plants or plant
35 propagation materials (preferably seeds) by the pests.

In the method of combating harmful fungi depending on the type of compound and the desired effect, the application rates of the mixtures according to the invention are from 0,3 g/ha to 2000 g/ha, preferably 5 g/ha to 2000 g/ha, more preferably from 50 to 900
40 g/ha, in particular from 50 to 750 g/ha.

In the method of combating animal pests (insects, acarids or nematodes) depending on the type of compound and the desired effect, the application rates of the mixtures according to the invention are from 0,3 g/ha to 2000 g/ha, preferably 5 g/ha to 2000 g/ha, more preferably from 50 to 900 g/ha, in particular from 50 to 750 g/ha.

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The inventive mixtures or compositions of these mixtures can also be employed for protecting plants from attack or infestation by animal pests (insects, acarids or nematodes) comprising contacting a plant, or soil or water in which the plant is growing.

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In the context of the present invention, the term plant refers to an entire plant, a part of the plant or the propagation material of the plant.

Plants and as well as the propagation material of said plants, which can be treated with the inventive mixtures include all genetically modified plants or transgenic plants, e.g. crops which tolerate the action of herbicides or fungicides or insecticides owing to breeding, including genetic engineering methods, or plants which have modified characteristics in comparison with existing plants, which can be generated for example by traditional breeding methods and/or the generation of mutants, or by recombinant procedures.

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For example, mixtures according to the present invention can be applied (as seed treatment, spray treatment, in furrow or by any other means) also to plants which have been modified by breeding, mutagenesis or genetic engineering including but not limited to agricultural biotech products on the market or in development (cf. http://www.bio.org/speeches/pubs/er/agri_products.asp). Genetically modified plants are plants, which genetic material has been so modified by the use of recombinant DNA techniques that under natural circumstances cannot readily be obtained by cross breeding, mutations or natural recombination. Typically, one or more genes have been integrated into the genetic material of a genetically modified plant in order to improve certain properties of the plant. Such genetic modifications also include but are not limited to targeted post-translational modification of protein(s), oligo- or polypeptides e. g. by glycosylation or polymer additions such as prenylated, acetylated or farnesylated moieties or PEG moieties.

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Plants that have been modified by breeding, mutagenesis or genetic engineering, e. g. have been rendered tolerant to applications of specific classes of herbicides, such as hydroxyphenylpyruvate dioxygenase (HPPD) inhibitors; acetolactate synthase (ALS) inhibitors, such as sulfonyl ureas (see e. g. US 6,222,100, WO 01/82685, WO 00/26390, WO 97/41218, WO 98/02526, WO 98/02527, WO 04/106529, WO 05/20673, WO 03/14357, WO 03/13225, WO 03/14356, WO 04/16073) or imidazolinones (see e. g. US 6,222,100, WO 01/82685, WO 00/026390, WO 97/41218,

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WO 98/002526, WO 98/02527, WO 04/106529, WO 05/20673, WO 03/014357, WO 03/13225, WO 03/14356, WO 04/16073); enolpyruvylshikimate-3-phosphate synthase (EPSPS) inhibitors, such as glyphosate (see e. g. WO 92/00377); glutamine synthetase (GS) inhibitors, such as glufosinate (see e.g. EP-A 242 236, EP-A 242 246) or oxynil herbicides (see e. g. US 5,559,024) as a result of conventional methods of breeding or genetic engineering. Several cultivated plants have been rendered tolerant to herbicides by conventional methods of breeding (mutagenesis), e. g. Clearfield® summer rape (Canola, BASF SE, Germany) being tolerant to imidazolinones, e. g. imazamox. Genetic engineering methods have been used to render cultivated plants such as soybean, cotton, corn, beets and rape, tolerant to herbicides such as glyphosate and glufosinate, some of which are commercially available under the trade names RoundupReady® (glyphosate-tolerant, Monsanto, U.S.A.) and LibertyLink® (glufosinate-tolerant, Bayer CropScience, Germany).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more insecticidal proteins, especially those known from the bacterial genus *Bacillus*, particularly from *Bacillus thuringiensis*, such as δ -endotoxins, e. g. CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) or Cry9c; vegetative insecticidal proteins (VIP), e. g. VIP1, VIP2, VIP3 or VIP3A; insecticidal proteins of bacteria colonizing nematodes, e. g. *Photorhabdus* spp. or *Xenorhabdus* spp.; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins, or other insect-specific neurotoxins; toxins produced by fungi, such *Streptomyces* toxins, plant lectins, such as pea or barley lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin or papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 3-hydroxysteroid oxidase, ecdysteroid-IDP-glycosyl-transferase, cholesterol oxidases, ecdysone inhibitors or HMG-CoA-reductase; ion channel blockers, such as blockers of sodium or calcium channels; juvenile hormone esterase; diuretic hormone receptors (helicokinin receptors); stilben synthase, bibenzyl synthase, chitinases or glucanases. In the context of the present invention these insecticidal proteins or toxins are to be understood expressly also as pre-toxins, hybrid proteins, truncated or otherwise modified proteins. Hybrid proteins are characterized by a new combination of protein domains, (see, e. g. WO 02/015701). Further examples of such toxins or genetically modified plants capable of synthesizing such toxins are disclosed, e. g., in EP-A 374 753, WO 93/007278, WO 95/34656, EP-A 427 529, EP-A 451 878, WO 03/18810 und WO 03/52073. The methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e. g. in the publications mentioned above. These insecticidal proteins contained in the genetically modified plants impart to the plants producing these proteins tolerance to harmful pests from all taxonomic groups of athropods, especially to beetles (Coeloptera), two-winged insects (Diptera), and moths (Lepidoptera) and to nematodes (Nematoda). Genetically modified plants capable to

synthesize one or more insecticidal proteins are, e. g., described in the publications mentioned above, and some of which are commercially available such as YieldGard® (corn cultivars producing the Cry1Ab toxin), YieldGard® Plus (corn cultivars producing Cry1Ab and Cry3Bb1 toxins), Starlink® (corn cultivars producing the Cry9c toxin), Herculex® RW (corn cultivars producing Cry34Ab1, Cry35Ab1 and the enzyme Phosphinothricin-N-Acetyltransferase [PAT]); NuCOTN® 33B (cotton cultivars producing the Cry1Ac toxin), Bollgard® I (cotton cultivars producing the Cry1Ac toxin), Bollgard® II (cotton cultivars producing Cry1Ac and Cry2Ab2 toxins); VIPCOT® (cotton cultivars producing a VIP-toxin); NewLeaf® (potato cultivars producing the Cry3A toxin); Bt-Xtra®, NatureGard®, KnockOut®, BiteGard®, Protecta®, Bt11 (e. g. Agrisure® CB) and Bt176 from Syngenta Seeds SAS, France, (corn cultivars producing the Cry1Ab toxin and PAT enzyme), MIR604 from Syngenta Seeds SAS, France (corn cultivars producing a modified version of the Cry3A toxin, c.f. WO 03/018810), MON 863 from Monsanto Europe S.A., Belgium (corn cultivars producing the Cry3Bb1 toxin), IPC 531 from Monsanto Europe S.A., Belgium (cotton cultivars producing a modified version of the Cry1Ac toxin) and 1507 from Pioneer Overseas Corporation, Belgium (corn cultivars producing the Cry1F toxin and PAT enzyme).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the resistance or tolerance of those plants to bacterial, viral or fungal pathogens. Examples of such proteins are the so-called "pathogenesis-related proteins" (PR proteins, see, e. g. EP-A 392 225), plant disease resistance genes (e. g. potato cultivars, which express resistance genes acting against *Phytophthora infestans* derived from the mexican wild potato *Solanum bulbocastanum*) or T4-lysozym (e. g. potato cultivars capable of synthesizing these proteins with increased resistance against bacteria such as *Erwinia amylovora*). The methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e. g. in the publications mentioned above.

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the productivity (e. g. bio mass production, grain yield, starch content, oil content or protein content), tolerance to drought, salinity or other growth-limiting environmental factors or tolerance to pests and fungal, bacterial or viral pathogens of those plants.

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve human or animal nutrition, e. g. oil crops that produce health-promoting long-chain omega-3 fatty acids or unsaturated omega-9 fatty acids (e. g. Nexera® rape, DOW Agro Sciences, Canada).

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve raw material production, e. g. potatoes that produce increased amounts of amylopectin (e. g. Amflora® potato, BASF SE, Germany).

Water-soluble concentrates (LS), flowable concentrates (FS), powders for dry treatment (DS), water-dispersible powders for slurry treatment (WS), water-soluble powders (SS), emulsions (ES) emulsifiable concentrates (EC) and gels (GF) are usually employed for the purposes of treatment of plant propagation materials, particularly seeds.

In a preferred embodiment of the invention, the inventive mixtures are used for the protection of the seed and the seedlings' roots and shoots, preferably the seeds.

Seed treatment can be made into the seedbox before planting into the field.

For seed treatment purposes, the weight ration in the binary, ternary and quaternary mixtures of the present invention generally depends from the properties of the compounds of the inventive mixtures.

Compositions, which are especially useful for seed treatment are e.g.:

- A Soluble concentrates (SL, LS)
- D Emulsions (EW, EO, ES)
- E Suspensions (SC, OD, FS)
- F Water-dispersible granules and water-soluble granules (WG, SG)
- G Water-dispersible powders and water-soluble powders (WP, SP, WS)
- H Gel-Formulations (GF)
- I Dustable powders (DP, DS)

These compositions can be applied to plant propagation materials, particularly seeds, diluted or undiluted. These compositions can be applied to plant propagation materials, particularly seeds, diluted or undiluted. The compositions in question give, after two-to-tenfold dilution, active substance concentrations of from 0.01 to 60% by weight, preferably from 0.1 to 40% by weight, in the ready-to-use preparations. Application can be carried out before or during sowing. Methods for applying or treating agrochemical compounds and compositions thereof, respectively, on to plant propagation material, especially seeds, are known in the art, and include dressing, coating, pelleting, dusting and soaking application methods of the propagation material (and also in furrow treatment). In a preferred embodiment, the compounds or the compositions thereof, respectively, are applied on to the plant propagation material by a method such that germination is not induced, e. g. by seed dressing, pelleting, coating and dusting.

In the treatment of plant propagation material (preferably seed), the application rates of the inventive mixture are generally for the formulated product (which usually comprises from 10 to 750 g/l of the active(s)) .

The invention also relates to the propagation products of plants, and especially the plant propagation material (preferably seed) comprising, that is, coated with and/or containing, a mixture as defined above or a composition containing the mixture of two or more active ingredients or a mixture of two or more compositions each providing one of the active ingredients. The plant propagation material (preferably seed) comprises the inventive mixtures in an amount of from 0.1 g to 10 kg per 100 kg of plant propagation material (preferably seed).

For example, the ratio by weight of compound I is herein preferably between 0,1 – 200 g/100kg plant propagation material (preferably seed), more preferred 1 to 200 g/100kg plant propagation material (preferably seed) and most preferred 1 to 100 g/100kg plant propagation material (preferably seed).

For example, the ratio by weight for compound II (such as triticonazole) or III (such as thiophanate-methyl, prochloraz, metalaxyl, dimethomorph) is herein preferably between 1 - 200 g/100kg plant propagation material (preferably seed), more preferred 5 to 200 g/100kg plant propagation material (preferably seed) and most preferred 5 to 100 g/100kg plant propagation material (preferably seed).

For example, the ratio by weight for compound III (such as N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-[2-(4'-trifluoromethylthio)-biphenyl]-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazole-4-carboxamide (common name bixafen), N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (sedaxane), N-[1,2,3,4-tetrahydro-9-(1-methylethyl)-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (common name: isopyrazam) and N-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxamide (common name: penthiopyrad)) is herein preferably between 1 - 200 g/100kg plant propagation material (preferably seed), more preferred 5 to 200 g/100kg plant propagation material (preferably seed), and most preferred 5 to 100g/100kg plant propagation material (preferably seed).

For example, the ratio by weight for compound III (such as azoxystrobin, pyraclostrobin, trifloxystrobin or orysastrobin (in particular orysastrobin)) is herein preferably between 1 - 200 g/100kg plant propagation material (preferably seed), more preferred 1 to 50 g/100kg plant propagation material (preferably seed) and most preferred 1 to 20 g/100kg plant propagation material (preferably seed).

The separate or joint application of the compounds of the inventive mixtures is carried out by spraying or dusting the seeds, the seedlings, the plants or the soils before or after sowing of the plants or before or after emergence of the plants.

The inventive mixtures are effective through both contact (via soil, glass, wall, bed net, carpet, plant parts or animal parts), and ingestion (bait, or plant part) and through trophallaxis and transfer.

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Preferred application methods are into water bodies, via soil, cracks and crevices, pastures, manure piles, sewers, into water, on floor, wall, or by perimeter spray application and bait.

- 10 According to another preferred embodiment of the invention, for use against non crop pests such as ants, termites, wasps, flies, mosquitoes, crickets, locusts, or cockroaches the inventive mixtures are prepared into a bait preparation.

- 15 The bait can be a liquid, a solid or a semisolid preparation (e.g. a gel). The bait employed in the composition is a product which is sufficiently attractive to incite insects such as ants, termites, wasps, flies, mosquitoes, crickets etc. or cockroaches to eat it. This attractant may be chosen from feeding stimulants or para and / or sex pheromones readily known in the art.

- 20 Methods to control infectious diseases transmitted by insects (e.g. malaria, dengue and yellow fever, lymphatic filariasis, and leishmaniasis) with the inventive mixtures and their respective compositions also comprise treating surfaces of huts and houses, air spraying and impregnation of curtains, tents, clothing items, bed nets, tsetse-fly trap or the like. Insecticidal compositions for application to fibers, fabric, knitgoods, non-
25 wovens, netting material or foils and tarpaulins preferably comprise a composition including the inventive mixtures, optionally a repellent and at least one binder.

- The inventive mixtures and the compositions comprising them can be used for protecting wooden materials such as trees, board fences, sleepers, etc. and buildings such as
30 houses, outhouses, factories, but also construction materials, furniture, leathers, fibers, vinyl articles, electric wires and cables etc. from ants and/or termites, and for controlling ants and termites from doing harm to crops or human being (e.g. when the pests invade into houses and public facilities).

- 35 In the case of soil treatment or of application to the pests dwelling place or nest, the quantity of active ingredient ranges from 0.0001 to 500 g per 100 m², preferably from 0.001 to 20 g per 100 m².

- 40 Customary application rates in the protection of materials are, for example, from 0.01 g to 1000 g of active compound per m² treated material, desirably from 0.1 g to 50 g per m².

Insecticidal compositions for use in the impregnation of materials typically contain from 0.001 to 95 weight %, preferably from 0.1 to 45 weight %, and more preferably from 1 to 25 weight % of at least one repellent and / or insecticide.

- 5 For use in bait compositions, the typical content of active ingredient is from 0.0001 weight % to 15 weight %, desirably from 0.001 weight % to 5% weight % of active compound. The composition used may also comprise other additives such as a solvent of the active material, a flavoring agent, a preserving agent, a dye or a bitter agent. Its attractiveness may also be enhanced by a special color, shape or texture.

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For use in spray compositions, the content of the mixture of the active ingredients is from 0.001 to 80 weights %, preferably from 0.01 to 50 weight % and most preferably from 0.01 to 15 weight %.

Claims

1. Mixtures comprising, as active components,
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- 1) an insecticidal compound I selected from following nicotinic receptor agonists/antagonists compounds: acetamiprid, clothianidin, dinotefuran, imidacloprid, thiamethoxam, nitenpyram; and
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- 2) one fungicidal compound(s) II selected from the group consisting of the azoles triticonazole, fluquinconazole, prothioconazole, difenoconazole, ipconazole, flutriafol and tebuconazole;
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- 3) one or two further fungicidal compound(s) III selected from the group consisting of thiophanate-methyl, prochloraz, pyraclostrobin, azoxystrobin, trifloxystrobin, orysastrobin, metalaxyl, dimethomorph, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-[2-(4'-trifluoromethylthio)-biphenyl]-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazole-4-carboxamide (common name bixafen), N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (common name: sedaxane), N-[1,2,3,4-tetrahydro-9-(1-methylethyl)-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide (common name: isopyrazam) and N-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxamide (common name: penthiopyrad);
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- in synergistic effective amounts.
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2. The mixture according to claim 1, comprising clothianidin imidacloprid or thiamethoxam as compound I.
3. The mixture according to any of claims 1 to 2, comprising triticonazole as compound II.
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4. The mixture according to any of claims 1 to 3, comprising one or two further fungicidal compound(s) III selected from the group consisting of thiophanate-methyl, prochloraz, pyraclostrobin, orysastrobin, metalaxyl, N-(3',4',5'-trifluorobiphenyl-2-

- 5 yl)- 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-[2-(1,3-dimethylbutyl)-phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, and N-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxamide (common name: pen thiopyrad).
- 10 5. The mixture according to any of claims 1 to 3, comprising comprising one or two further fungicidal compound(s) III selected from the group consisting of prochloraz, pyraclostrobin, orysastrobin, metalaxyl and N-(3',4',5'-trifluorobiphenyl-2-yl)- 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide.
- 15 6. The mixture according to claim 1, comprising imidacloprid or clothianidin as compound I, triticonazole as compound II, pyraclostrobin and metalaxyl as compounds III.
7. The mixture according to claim 1, comprising thiamethoxam, triticonazole and prochloraz.
- 20 8. The mixture according to claim 1, comprising imidacloprid or clothianidin as compound I, triticonazole as compound II, pyraclostrobin and prochloraz as compounds III.
- 25 9. Mixtures comprising, as active components,
 1) an insecticidal compound I selected from acetamiprid; and
 2) triticonazole.
 in synergistic effective amounts.
- 30 10. A pesticidal composition, comprising a liquid or solid carrier and a mixture as defined in any of claims 1 to 9.
- 35 11. A method for controlling pests and/or improving the health of plants, wherein
 (a) the pest, their habitat, breeding grounds, their locus or the plants to be protected against pest attack, the soil or plant propagation material; or
 (b) the plant, the locus where the plant is growing or is expected to grow or
 plant propagation material from which the plant grows;
 are treated with an effective amount of a mixture as defined in any of claims 1 to 9.
- 40 12. A method for protection of plant propagation material from pests comprising contacting the plant propagation materials with a mixture as defined in any of claims 1 to 9 in pesticidally effective amounts.

13. A method as claimed in claim 12, wherein the mixture as defined in any of claims 1 to 9 is applied in an amount of from 0.01 g to 10 kg per 100 kg of plant propagation materials.
- 5 14. A method as claimed in claims 11 to 13, wherein compound I and compounds II as defined in any of claims 1 to 9 are applied simultaneously, that is jointly or separately, or in succession.
- 10 15. Plant propagation material, comprising the mixture as defined in any of claims 1 to 9 in an amount of from 0.01 g to 10 kg per 100 kg of plant propagation material.