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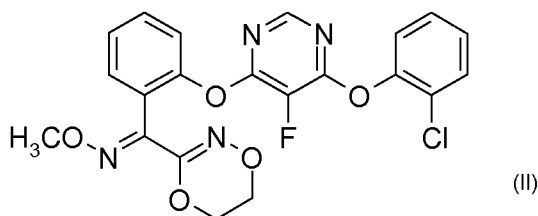
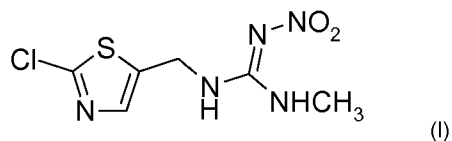
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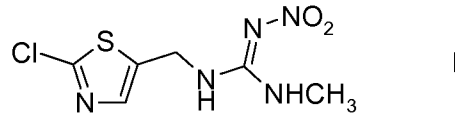
(57) Abstract: Pesticidal mixtures, comprising a) clothianidine of formula (I) and b) fluoxastrobin of formula (II) in synergistically effective amounts, plant-protecting mixtures, compositions containing the mixtures, and to methods for controlling or preventing fungal infestation or harmful insects or nematodes in plants, and methods of improving the health of plants by applying said mixtures to the plants or the locus thereof.

Pesticidal mixtures

Description

5 The present invention relates to pesticidal mixtures comprising

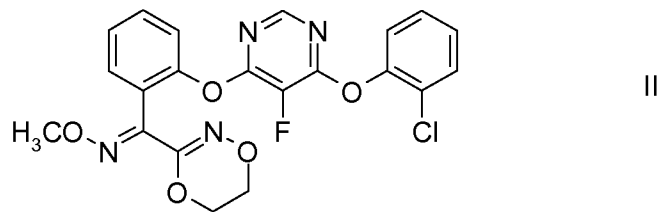
a) clothianidine of the formula I,



and

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b) fluoxastrobin of the formula II,



in synergistically effective amounts.

15 Moreover, the invention relates to a method for controlling phytopathogenic harmful fungi using mixtures of the compound I with the compound II and to the use of the compound I with the compound II for preparing such mixtures and compositions comprising these mixtures.

20 The present invention also relates to plant-protecting mixtures and to a method of improving the health of plants by applying said mixtures to the plants or the locus thereof.

25 Furthermore, the invention relates to a method of controlling fungi and/or improving the health of plants, which comprises treating a site, for example a plant or a plant propagation material, that is infested or liable to be infested by fungi with the pesticides present in a inventive mixture in any desired sequence or simultaneously, that is, jointly or separately.

30 Furthermore, the invention relates to a method of controlling harmful insects or nematodes, which comprises treating a site, for example a plant or a plant propagation material, that is infested or liable to be infested by said pests with the pesticides present in a inventive mixture in any desired sequence or simultaneously, that is, jointly or

separately.

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 and pathogen control.

Another problem encountered concerns the need to have available pest control agents which are effective against a broad spectrum of pests and pathogens.

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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". 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.

25 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 or pathogens that have developed natural or adapted resistance against the active compound in question.

30 It was therefore an object of the present invention to provide pesticidal mixtures which solve the problems outlined above.

The combating of harmful phytopathogenic fungi is not the only problem the farmer has to face. Also harmful insects and other pests can cause a great damage to crops and other plants. An efficient combination of fungicidal and insecticidal activity is desirable to overcome this problem. Thus, it is a further object of the present invention to provide a mixture that, on the one hand, has good fungicidal activity, and, on the other hand, good insecticidal activity, resulting in a broader pesticidal spectrum of action.

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We have found that this object is in part or in whole achieved by the combination of active compounds defined in the outset.

5 Especially, it has been found that a mixture of the compound of formula I and the compound of formula II as defined in the outset show markedly enhanced action against plant pathogens 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.

10 It has been found that the action of the inventive mixtures, e.g. of the mixture of the compound of formula I and the compound of formula II as defined in the outset, goes far beyond the fungicidal and insecticidal action of the active compounds present in the mixture alone. It has been shown that the mixtures exhibit plant health effects in the frame of the present invention. The term plant health comprises various sorts of
15 improvements of plants that are not connected to the control of pests.

The compound I, (E)-1-(2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine, its preparation and its action against pests is known from the literature (EP-A 376 279; common name clothianidine).

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The compound II, (E)-{2-[6-(2-chlorophenoxy)-5-fluoropyrimidin-4-yloxy]phenyl}{5,6-dihydro-1,4,2-dioxazin-3-yl)methanone O-methyloxime, its preparation and its action against harmful fungi is likewise known from the literature (WO 97/27189; common name fluoxastrobin).

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Mixtures of clothianidine I and fluoxastrobin II are embraced by the general disclosure of WO 00/30440, but are not explicitly disclosed.

30 The compounds of formulae I and II are capable of forming salts or adducts with inorganic or organic acids or with metal ions.

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

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Suitable organic acids are, for example, formic acid, carbonic acid and alkanoic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glycolic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic

acid, p-toluenesulfonic acid, salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid or 2-acetoxybenzoic acid.

Suitable metal ions are in particular the ions of the elements of the first to eighth transition group, especially chromium, manganese, iron, cobalt, nickel, copper, zinc, and additionally those of the second main group, especially calcium and magnesium, and of the third and fourth main group, in particular aluminum, tin and lead. If appropriate, the metals can be present in the different valencies that they can assume.

The active compounds mentioned above can also be employed in the form of their agriculturally compatible salts. These are usually the alkali metal or alkaline earth metal salts, such as sodium, potassium or calcium salts.

In a preferred embodiment of the invention, mixtures of the compound of formula I and the compound of formula II are used. Under certain conditions, it may be advantageous to combine the mixture with further active compounds III. Mixtures of three or more compounds may be suitable.

When preparing the mixtures, preference is given to using the pure active compounds which, if required, may be mixed with further active compounds III against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers as further active components.

Preferred further fungicides III are those selected from the group consisting of

- strobilurins, such as azoxystrobin, dimoxystrobin, enestroburin, kresoxim-methyl, methominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyribencarb, trifloxystrobin, 2-(ortho-((2,5-dimethylphenyl-oxymethylene)phenyl)-3-methoxy-acrylic acid methyl ester;
- carbonic acid amides, such as anilides: benalaxyl, benalaxyl-M, benodanil, bixafen, boscalid, carboxin, carpropamid, diclocymet, fenfuram, fenhexamid, flutolanil, furametpyr, isotianil, kiralaxyl, mandipropamid, mepronil, metalaxyl, ofurace, oxadixyl, oxycarboxin, penthiopyrad, silthiofam, thifluzamide, tiadinil, N-(3',4'-dichloro-5-fluoro-biphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide, N-(2-(1,3-dimethyl-butyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxylic acid amide, N-(4'-chloro-3',5-difluoro-biphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide, N-(4'-chloro-3',5-difluoro-biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide, N-(3',4'-dichloro-5-fluoro-biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide,

- N-(3',5-difluoro-4'-methyl-biphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide, N-(3',5-difluoro-4'-methyl-biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide, N-(2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide, N-(cis-2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide, N-(trans-2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid amide;
- carbonic acid morpholides: dimethomorph, flumorph;
- benzoic acid amides: flumetover, fluopicolide, fluopyram, zoxamide;
- 10 • azoles, such as triazoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazol, imibenconazole, ipconazole, metconazol, myclobutanil, oxpoconazol, paclobutrazol, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon,
- 15 triadimenol, triticonazole;
- imidazoles: cyazofamid, imazalil, pefurazoate, prochloraz, triflumizole;
- benzimidazoles: benomyl, carbendazim, fuberidazole, thiabendazole;
- others: ethaboxam, etridiazole, hymexazole, 1-(4-chloro-phenyl)-1-(propin-2-yloxy)-3-(4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl)-propan-2-one;
- 20 • nitrogen containing heterocycles, such as pyridines: fluazinam, pyrifenox, 3-[5-(4-chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine;
- pyrimidines: bupirimate, cyprodinil, diflumetorim, fenarimol, ferimzone, mepanipyrim, nitrapyrin, nuarimol, pyrimethanil;
- pyrroles: fenpiclonil, fludioxonil;
- 25 morpholines: aldimorph, dodemorph, fenpropimorph, tridemorph;
- dicarboximides: fluoroimid, iprodione, procymidone, vinclozolin;
- non-aromatic five-membered rings: famoxadone, fenamidone, othilinone, probenazole;
- others: acibenzolar-S-methyl, amisulbrom, anilazin, blasticidin-S, captafol, captan,
- 30 chinomethionat, dazomet, debacarb, diclomezine, fenoxanil, fenpropidin, folpet, piperalin, proquinazid, pyroquilon, quinoxifen, triazoxid, tricyclazole, tricyclazole, triforine, 5-chloro-7-(4-methyl-piperidin-1-yl)-6-(2,4,6-trifluoro-phenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, 2-butoxy-6-iodo-3-propyl-chromen-4-one
- carbamates and dithiocarbamates, such as: dithiocarbamates: ferbam, mancozeb,
- 35 maneb, metam, metiram, propineb, thiram, zineb, ziram;
- carbamates: diethofencarb, flubenthiavalecarb, iprovalicarb, propamocarb, valiphenal, N-(1-(1-(4-cyanophenyl)ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester;
- guanidines, such as: dodine, guazatine, iminoctadine;

- antibiotics: kasugamycin, polyoxine, streptomycin, validamycin A;
- organometal compounds: fentin salts (e.g. fentin acetate, fentin chloride, fentin hydroxide);
- sulphur containing heterocycles, such as: dithianon, isoprothiolane;
- 5 • organophosphorous compounds, such as: edifenphos, fosetyl, fosetyl-aluminium, iprobenfos, pyrazophos, tolclofos-methyl;
- organochloro compounds, such as: chlorothalonil, dichlofluanid, dichlorophen, flusulfamide, hexachlorbenzene, pencycuron, phthalide, quintozone, thiophanate-methyl, tolylfluanid;
- 10 • inorganic compounds, such as: sulphur, phosphorous acid (H_3PO_3) and its salts, copper salts, e. g. bordeaux mixture, copper acetate, copper hydroxide, copper oxychloride, basic copper sulphate;
- nitrophenyl derivatives, such as: binapacryl, dicloran, dinobuton, dinocap, tecnazen;
- growth retardants: prohexadione and its salts, trinexapac-ethyl, chlormequat,
- 15 mepiquat-chloride and diflufenzopyr;
- others: bronopol, cyflufenamid, cymoxanil, diphenylamin, metrafenone, mildiomyacin, spiroxamine, tolylfluanid, N-(cyclopropylmethoxyimino-(6-difluoromethoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide.
- 20 More preferred further fungicides are those selected from the group consisting of
 - azoles: benomyl, difenoconazole, epoxiconazole, fluquinconazole, flutriafol, hymexazole, imazalil, metconazole, prothioconazole, tebuconazole; thiabendazole, triadimenol, prochloraz, triticonazole, carbendazim;
 - strobilurins: azoxystrobin, kresoxim-methyl, orysastrobin, pyraclostrobin, trifloxystrobin;
 - 25 • carboxamides, such as boscalid, carboxin, metalaxyl, oxadixyl, dimethomorph; silthiofam, mandipropamid;
 - heterocyclic compounds, such as fludioxonil; captan, dazomet, pyrimethanil; iprodione;
 - carbamates, such as mancozeb, maneb, metiram, thiram;
 - 30 • other active compounds, selected from inorganic active compounds: sulphur, Bordeaux mixture, copper acetate, copper hydroxide, copper oxychloride, basic copper sulfate; others: guazatine, streptomycin.

Preferred further insecticides III are those selected from the groups consisting of

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A.1. Organo(thio)phosphates: acephate, azamethiphos, azinphos-ethyl, azinphos-methyl, chlorethoxyfos, chlorfenvinphos, chlormephos, chlorpyrifos, chlorpyrifos-methyl, coumaphos, cyanophos, demeton-S-methyl, diazinon, dichlorvos/ DDVP, dicrotophos, dimethoate, dimethylvinphos, disulfoton, EPN, ethion, ethoprophos, famphur,

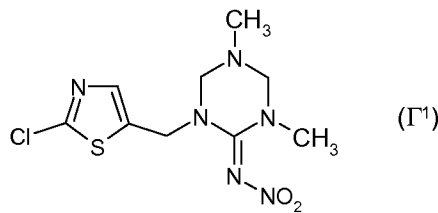
fenamiphos, fenitrothion, fenthion, flupyrazophos, fosthiazate, heptenophos, isoxathion, malathion, mecarbam, methamidophos, methidathion, mevinphos, monocrotophos, naled, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, phoxim, pirimiphos-methyl, profenofos, propetamphos, prothiofos, pyraclofos, pyridaphenthion, quinalphos, sulfotep, tebupirimfos, temephos, terbufos, tetrachlorvinphos, thiometon, triazophos, trichlorfon, vamidothion;

A.2. Carbamates: aldicarb, alanycarb, bendiocarb, benfuracarb, butocarboxim, butoxycarboxim, carbaryl, carbofuran, carbosulfan, ethiofencarb, fenobucarb, formetanate, furathiocarb, isoprocarb, methiocarb, methomyl, metolcarb, oxamyl, pirimicarb, propoxur, thiodicarb, thiofanox, trimethacarb, XMC, xylylcarb, triazamate;

A.3. Pyrethroids: acrinathrin, allethrin, d-cis-trans allethrin, d-trans allethrin, bifenthrin, bioallethrin, bioallethrin S-cyclopentenyl, bioresmethrin, cycloprothrin, cyfluthrin, beta-, yfluthrin, cyhalothrin, lambda-cyhalothrin, gamma-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, theta-cypermethrin, zeta-cypermethrin, cyphenothrin, deltamethrin, empenethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, flumethrin, tau-fluvalinate, halfenprox, imiprothrin, permethrin, phenothrin, prallethrin, resmethrin, RU 15525, silafluofen, tefluthrin, tetramethrin, tralomethrin, transfluthrin, ZXI 8901;

A.4. Juvenile hormone mimics: hydroprene, kinoprene, methoprene, fenoxycarb, pyriproxyfen;

A.5. Nicotinic receptor agonists/antagonists compounds: acetamiprid, bensultap, cartap hydrochloride, dinotefuran, imidacloprid, thiamethoxam, nitenpyram, nicotine, spinosad (allosteric agonist), thiacloprid, thiocyclam, thiosultap-sodium, the thiazol compound of formula (Γ^1)



A.6. GABA gated chloride channel antagonist compounds: chlordane, endosulfan, gamma-HCH (lindane); acetoprole, ethiprole, fipronil, pyrafluprole, pyriprole, vaniliprole, 5-Amino-1-(2,6-dichloro-4-trifluoromethyl-phenyl)-4-trifluoromethanesulfinyl-1H-pyrazole-3-carbothioic acid amide

A.7. Chloride channel activators: abamectin, emamectin benzoate, milbemectin, lepimectin;

A.8. METI I compounds: fenazaquin, fenpyroximate, pyrimidifen, pyridaben, tebufenpyrad, tolfenpyrad, flufenerim, rotenone;

A.9. METI II and III compounds: acequinocyl, fluacyprim, hydramethylnon;

- A.10. Uncouplers of oxidative phosphorylation: chlorfenapyr, DNOC;
- A.11. Inhibitors of oxidative phosphorylation: azocyclotin, cyhexatin, diafenthiuron, fenbutatin oxide, propargite, tetradifon;
- A.12. Moulting disruptors: cyromazine, chromafenozide, halofenozide, methoxyfenozide, 5 tebufenozide;
- A.13. Synergists: piperonyl butoxide, tribufos;
- A.14. Sodium channel blocker compounds: indoxacarb, metaflumizone;
- A.15. Fumigants: methyl bromide, chloropicrin sulfuryl fluoride;
- A.16. Selective feeding blockers: crylotie, pymetrozine, flonicamid;
- 10 A.17. Mite growth inhibitors: clofentezine, hexythiazox, etoxazole;
- A.18. Chitin synthesis inhibitors: buprofezin, bistrifluron, chlorfluazuron, diflubenzuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, noviflumuron, teflubenzuron, triflumuron;
- A.19. Lipid biosynthesis inhibitors: spiroticlofen, spiromesifen, spirotetramat;
- 15 A.20. octapaminergic agonsits: amitraz;
- A.21. ryanodine receptor modulators: flubendiamide;
- A.22. Various: aluminium phosphide, amidoflumet, benclothiaz, benzoximate, bifenazate, borax, bromopropylate, cyanide, cyenopyrafen, cyflumetofen, chinomethionate, dicofol, fluoroacetate, phosphine, pyridalyl, pyrifluquinazon, sulfur, 20 tartar emetic;
- A.23. N-R'-2,2-dihalo-1-R''cyclo-propanecarboxamide-2-(2,6-dichloro- α,α,α -tri-fluoro-p-tolyl)hydrazone or N-R'-2,2-di(R''')propionamide-2-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)-hydrazone, wherein R' is methyl or ethyl, halo is chloro or bromo, R'' is hydrogen or methyl and R''' is methyl or ethyl;
- 25 A.24. Anthranilamides: chloranthraniliprole, 5-Bromo-2-(3-chloro-pyridin-2-yl)-2H-pyrazole-3-carboxylic acid (4-cyano-2-methyl-6-methylcarbamoyl-phenyl)-amide;
- A.25. Malononitrile compounds: $\text{CF}_3(\text{CH}_2)_2\text{C}(\text{CN})_2\text{CH}_2(\text{CF}_2)_3\text{CF}_2\text{H}$, $\text{CF}_3(\text{CH}_2)_2\text{C}(\text{CN})_2\text{CH}_2(\text{CF}_2)_5\text{CF}_2\text{H}$, $\text{CF}_3(\text{CH}_2)_2\text{C}(\text{CN})_2(\text{CH}_2)_2\text{C}(\text{CF}_3)_2\text{F}$, $\text{CF}_3(\text{CH}_2)_2\text{C}(\text{CN})_2(\text{CH}_2)_2(\text{CF}_2)_3\text{CF}_3$, $\text{CF}_2\text{H}(\text{CF}_2)_3\text{CH}_2\text{C}(\text{CN})_2\text{CH}_2(\text{CF}_2)_3\text{CF}_2\text{H}$, 30 $\text{CF}_3(\text{CH}_2)_2\text{C}(\text{CN})_2\text{CH}_2(\text{CF}_2)_3\text{CF}_3$, $\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{C}(\text{CN})_2\text{CH}_2(\text{CF}_2)_3\text{CF}_2\text{H}$, and $\text{CF}_3\text{CF}_2\text{CH}_2\text{C}(\text{CN})_2\text{CH}_2(\text{CF}_2)_3\text{CF}_2\text{H}$;
- A.26. Microbial disruptors: *Bacillus thuringiensis* subsp. *Israelensi*, *Bacillus sphaericus*, *Bacillus thuringiensis* subsp. *Aizawai*, *Bacillus thuringiensis* subsp. *Kurstaki*, *Bacillus thuringiensis* subsp. *Tenebrionis*.

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A preferred embodiment of the invention relates to mixtures of the compounds of formulae I and II with a compound III from the group of the carbamates as defined above. Carbamates are preferably selected from carbofuran, carbosulfan, and thiodicarb.

Another preferred embodiment of the invention relates to mixtures of the compounds of formulae I and II with a compound III from the group of the pyrethroids as defined above. Pyrethroids are preferably selected from bifenthrin, cyfluthrin, cypermethrin, alpha-cypermethrin, and tefluthrin.

Another preferred embodiment of the invention relates to mixtures of the compounds of formulae I and II with a compound III from the group of the nicotinic receptor agonists/antagonists compounds as defined above. Nicotinic receptor agonists/antagonists compounds are preferably selected from acetamiprid, dinotefuran, imidacloprid, spinosad, thiamethoxam, and thiacloprid.

Another preferred embodiment of the invention relates to mixtures of the compounds of formulae I and II with a compound III from the group of the GABA gated chloride channel antagonist compounds as defined in the outset. A preferred GABA gated chloride channel antagonist compound is fipronil.

In one embodiment, the mixtures according to the invention are used for combating harmful fungi and harmful insects or nematodes.

In a further embodiment, the mixtures according to the invention are used for combating harmful fungi.

In a further embodiment, the mixtures according to the invention are used for combating harmful insects or nematodes.

In a further embodiment, the mixtures according to the invention are used for a method of controlling fungi and/or improving the health of plants, which comprises treating a site, for example a plant or a plant propagation material, that is infested or liable to be infested by fungi with the compound of formula I, and the compound II, in any desired sequence or simultaneously, that is, jointly or separately.

In a further embodiment, the mixtures according to the invention are used for a method of controlling harmful insects or nematodes, which comprises treating a site, for example a plant or a plant propagation material, that is infested or liable to be infested by fungi with the compound of formula I, and the compound II, in any desired sequence or simultaneously, that is, jointly or separately.

In a further embodiment, the mixtures according to the invention are used for a method of improving the health of plants, which comprises treating a site, for example a plant or a plant propagation material, that is infested or liable to be infested by fungi with the compound of formula I, and the compound II, in any desired sequence or
5 simultaneously, that is, jointly or separately.

In another embodiment of the method the application the compound of formula I, and the compound II, can be made in the absence of pest pressure.

10 In a further embodiment, the mixtures according to the invention comprise the compound of formula I and compound of formula II in a synergistic effective amount and are used for improving the health of plants. Such method can be applied under pest pressure or in the absence of pest pressure.

15 In a further preferred embodiment, the mixtures according to the invention are used for for foliar application in living crops of plants, for soil applications prior to sowing or planting, including overall soil treatment and furrow applications, as well as, in particular, for dressing applications on plant propagation material. The latter term embraces seeds of all kinds (fruit, tubers, grains), cuttings, cut shoots and the like. One particular field of
20 application is the treatment of all kinds of seeds.

The mixtures according to the invention are especially important for controlling a large number of fungi and insects or nematodes on a variety of crop plants such as wheat, corn, rye, barley, oats, sorghum, rice, maize, grass, bananas, cotton, soy beans, coffee,
25 sugar cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, drybeans, tomatoes, potatoes, lettuce, cucurbits, cabbage, carrots, cruciferous, sunflowers and cucurbits, and on the seeds of these plants or on pasture and on seeds of pasture. In a special embodiment the mixtures according to the present invention are applied on soybeans. In another preferred embodiment the mixtures according to
30 the present invention are applied on seeds. In a particular embodiment the mixtures according to the present invention are applied on seeds of soybeans.

Specifically, the mixtures are suitable for controlling each of the following harmful fungi:

- Alternaria species on vegetables, oilseed rape, sugar beet, cereals, fruit and rice,
35 such as, e.g. *A. solani* or *A. alternata* on potatoes and tomatoes,;
- Aphanomyces species on sugar beet and vegetables,
- Ascochyta species on cereals and vegetables, e.g. *Ascochyta tritici* on wheat,
- Bipolaris and Drechslera species on corn, cereals, rice and lawns, such as, e.g. *D. maydis* on corn,

- *Blumeria graminis* (powdery mildew) on cereals, e.g. wheat or barley,
- *Botrytis cinerea* (gray mold) on strawberries, vegetables, flowers, wheat and grapes,
- *Bremia lactucae* on lettuce,
- *Cercospora* species on corn, soybeans, rice and sugar beet, e.g. *Cercospora sojae* or *Cercospora kikuchii* on soybeans,
- *Cladosporium herbarum* on wheat,
- *Cochliobolus* species on corn, cereals, rice, such as, e.g. *Cochliobolus sativus* on cereals, *Cochliobolus miyabeanus* on rice,
- *Colletotricum* species on soybeans and cotton, e.g. *Colletotrichum truncatum* on soybeans,
- *Corynespora cassiicola* on soybeans,
- *Dematophora necatrix* on soybeans,
- *Diaporthe phaseolorum* on soybeans,
- *Drechslera* species, *Pyrenophora* species on corn, cereals, rice and lawns, such as, e.g. *D. teres* on barley or *D. tritici-repentis* on wheat,
- *Esca* on grapevines, caused by *Phaeoacremonium chlamydosporium*, *Ph. Aleophilum* and *Formitipora punctata* (syn. *Phellinus punctatus*);
- *Elsinoe ampelina* on wheat,
- *Entyloma oryzae* on rice,
- *Epicoccum* spp. on wheat,
- *Exserohilum* species on corn,
- *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* on cucumbers,
- *Fusarium* and *Verticillium* species on various plants, such as, e.g. *F. graminearum* or *F. culmorum* on cereals or *F. oxysporum* on a multitude of plants, such as, e.g. tomatoes, and *Fusarium solani* on soybeans,
- *Gaeumanomyces graminis* on cereals, e.g. wheat or barley,
- *Glomerella cingulata* on grapes and other crops,
- *Gibberella* species on cereals and rice (for example *Gibberella fujikuroi* on rice);
- Grainstaining complex on rice;
- *Guignardia budwelli* on grapes,
- *Helminthosporium* species on corn and rice,
- *Isariopsis clavispora* on grapes,
- *Macrophomina phaseolina* on soybeans,
- *Microdochium nivale* on cereals;
- *Microsphaera diffusa* on soybeans,
- *Mycosphaerella* species on cereals, bananas and groundnuts, such as, e.g., *M. graminicola* on wheat or *M. fijiensis* on bananas;
- *Peronospora* species on cabbage and bulbous plants, such as, e.g., *P. brassicae* on cabbage, *P. destructor* on onions, or *P. manshurica* on soybeans,

- *Phakopsara pachyrhizi* and *Phakopsara meibomia* on soybeans,
- *Phialophora gregata* on soybeans,
- *Phomopsis* species on sunflowers, soybeans (e.g. *P. phaseoli*) and grapes (e.g. *P. viticola*),
- 5 • *Phytophthora* species on various plants, such as, e.g. *P. capsici* on bell pepper, *P. megasperma* on soybeans, and *P. infestans* on potatoes and tomatoes,
- *Plasmopara viticola* on grapevines,
- *Podosphaera leucotricha* on apples,
- *Pseudocercospora herpotrichoides* on cereals (wheat or barley),
- 10 • *Pseudoperonospora* on various plants, such as, e.g. *P. cubensis* on cucumber or *P. humili* on hops,
- *Pseudopezizicola tracheiphilae* on grapes,
- *Puccinia* species on various plants, such as, e.g. *P. tritici*, *P. striiformis*, *P. hordei* or *P. graminis* on cereals (wheat or barley) or *P. asparagi* on asparagus,
- 15 • *Pyricularia oryzae*, *Corticium sasakii*, *Sarocladium oryzae*, *S. attenuatum*, *Entyloma oryzae* on rice,
- *Pyrenophora tritici-repentis* on wheat or *Pyrenophora teres* on barley,
- *Pyricularia grisea* on lawns and cereals,
- *Pythium* spp. on lawns, rice, corn, wheat, cotton, oilseed rape, sunflowers, sugar
- 20 beet, vegetables and other plants, such as, e.g. *P. ultimum* on various plants, *P. aphanidermatum* on lawns;
- *Ramularia collo-cygni* (physiological leaf spots) on barley,
- *Rhizoctonia* species on cotton, rice, potatoes, lawns, corn, oilseed rape, potatoes, sugar beet, vegetables and on various plants, such as, e.g. *R. solani* on beet and
- 25 various plants, and *Rhizoctonia cerealis* on wheat or barley,
- *Rhynchosporium secalis* on barley, rye and triticale,
- *Sclerotinia* species on oilseed rape and sunflowers, and e.g. *S. sclerotiorum* or *S. rolfsii* on soybeans,
- *Septoria glycines* on soybeans,
- 30 • *Septoria tritici* and *Stagonospora nodorum* on wheat,
- *Erysiphe* (syn. *Uncinula*) *necator* on grapevines,
- *Setosphaeria* species on corn and lawns,
- *Sphacelotheca reilina* on corn,
- *Stagonospora nodorum* on wheat,
- 35 • *Thielaviopsis* species on soybeans and cotton,
- *Tilletia* species on cereals,
- *Typhula incarnata* on wheat or barley,
- *Ustilago* species on cereals, corn and sugar cane, such as, e.g. *U. maydis* on corn,

- *Venturia* species (scab) on apples and pears, such as, for example, *V. inaequalis* on apples.

They are also suitable for controlling the following harmful insects from the order of the

- 5 • 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*,
10 *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*,
15 *Leucoptera scitella*, *Lithocolletis 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*
20 *scabra*, *Plutella xylostella*, *Pseudoplusia includens*, *Rhyacionia frustrana*, *Scrobipalpula absoluta*, *Sitotroga cerealella*, *Sparganothis pillariana*, *Spodoptera frugiperda*, *Spodoptera littoralis*, *Spodoptera litura*, *Thaumatopoea pityocampa*, *Tortrix viridana*, *Trichoplusia ni* and *Zeiraphera canadensis*,
- beetles (Coleoptera), for example *Agrilus sinuatus*, *Agriotes lineatus*, *Agriotes*
25 *obscurus*, *Amphimallus solstitialis*, *Anisandrus dispar*, *Anthonomus grandis*, *Anthonomus pomorum*, *Atomaria linearis*, *Blastophagus piniperda*, *Blitophaga undata*, *Bruchus rufimanus*, *Bruchus pisorum*, *Bruchus lentis*, *Byctiscus betulae*, *Cassida nebulosa*, *Cerotoma trifurcata*, *Ceuthorrhynchus assimilis*, *Ceuthorrhynchus napi*, *Chaetocnema tibialis*, *Conoderus vespertinus*, *Crioceris*
30 *asparagi*, *Diabrotica longicornis*, *Diabrotica 12-punctata*, *Diabrotica virgifera*, *Epilachna varivestis*, *Epitrix hirtipennis*, *Eutinobothrus brasiliensis*, *Hylobius abietis*, *Hypera brunneipennis*, *Hypera postica*, *Ips typographus*, *Lema bilineata*, *Lema melanopus*, *Leptinotarsa decemlineata*, *Limonius californicus*, *Lissorhoptrus oryzophilus*, *Melanotus communis*, *Meligethes aeneus*, *Melolontha hippocastani*,
35 *Melolontha melolontha*, *Oulema oryzae*, *Ortiorrhynchus sulcatus*, *Otiorrhynchus ovatus*, *Phaedon cochleariae*, *Phyllotreta chrysocephala*, *Phyllophaga* sp., *Phyllopertha horticola*, *Phyllotreta nemorum*, *Phyllotreta striolata*, *Popillia japonica*, *Sitona lineatus* and *Sitophilus granaria*,

- 5 dipterans (Diptera), for example *Aedes aegypti*, *Aedes vexans*, *Anastrepha ludens*, *Anopheles maculipennis*, *Ceratitis capitata*, *Chrysomya bezziana*, *Chrysomya hominivorax*, *Chrysomya macellaria*, *Contarinia sorghicola*, *Cordylobia anthropophaga*, *Culex pipiens*, *Dacus cucurbitae*, *Dacus oleae*, *Dasineura brassicae*, *Fannia canicularis*, *Gasterophilus intestinalis*, *Glossina morsitans*, *Haematobia irritans*, *Haplodiplosis equestris*, *Hylemyia platura*, *Hypoderma lineata*, *Liriomyza sativae*, *Liriomyza trifolii*, *Lucilia caprina*, *Lucilia cuprina*, *Lucilia sericata*, *Lycoria pectoralis*, *Mayetiola destructor*, *Musca domestica*, *Muscina stabulans*, *Oestrus ovis*, *Oscinella frit*, *Pegomya hysocyami*, *Phorbia antiqua*, *Phorbia brassicae*, *Phorbia coarctata*, *Rhagoletis cerasi*, *Rhagoletis pomonella*, *Tabanus bovinus*, *Tipula oleracea* and *Tipula paludosa*,
- 10 thrips (Thysanoptera), e.g. *Frankliniella fusca*, *Frankliniella occidentalis*, *Frankliniella tritici*, *Scirtothrips citri*, *Thrips oryzae*, *Thrips palmi* and *Thrips tabaci*,
- 15 hymenopterans (Hymenoptera), e.g. *Athalia rosae*, *Atta cephalotes*, *Atta sexdens*, *Atta texana*, *Hoplocampa minuta*, *Hoplocampa testudinea*, *Monomorium pharaonis*, *Solenopsis geminata* and *Solenopsis invicta*,
- 20 heteropterans (Heteroptera), 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* and *Thyanta perditor*,
- 25 homopterans (Homoptera), e.g. *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*, *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 pyramis*, *Metopolophium dirhodum*, *Myzodes 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*, and *Viteus vitifolii*.

- termites (Isoptera), e.g. *Calotermes flavicollis*, *Leucotermes flavipes*,
Reticulitermes lucifugus und *Termes natalensis*,
- orthopterans (Orthoptera), e.g. *Acheta domestica*, *Blatta orientalis*, *Blattella*
germanica, *Forficula auricularia*, *Gryllotalpa gryllotalpa*, *Locusta migratoria*,
5 *Melanoplus bivittatus*, *Melanoplus femur-rubrum*, *Melanoplus mexicanus*,
Melanoplus sanguinipes, *Melanoplus spretus*, *Nomadacris septemfasciata*,
Periplaneta americana, *Schistocerca americana*, *Schistocerca peregrina*,
Stauronotus maroccanus and *Tachycines asynamorus*,
- Arachnoidea, such as arachnids (Acarina), e.g. of the families Argasidae, Ixodidae
10 and Sarcoptidae, such as *Amblyomma americanum*, *Amblyomma variegatum*,
Argas persicus, *Boophilus annulatus*, *Boophilus decoloratus*, *Boophilus microplus*,
Dermacentor silvarum, *Hyalomma truncatum*, *Ixodes ricinus*, *Ixodes rubicundus*,
Ornithodoros moubata, *Otobius megnini*, *Dermanyssus gallinae*, *Psoroptes ovis*,
Rhipicephalus appendiculatus, *Rhipicephalus evertsi*, *Sarcoptes scabiei*, and
15 *Eriophyidae* spp. such as *Aculus schlechtendali*, *Phyllocoptrata oleivora* and
Eriophyes sheldoni; *Tarsonemidae* spp. such as *Phytonemus pallidus* and
Polyphagotarsonemus latus; *Tenuipalpidae* spp. such as *Brevipalpus phoenicis*;
Tetranychidae spp. such as *Tetranychus cinnabarinus*, *Tetranychus kanzawai*,
Tetranychus pacificus, *Tetranychus telarius* and *Tetranychus urticae*, *Panonychus*
20 *ulmi*, *Panonychus citri*, and *oligonychus pratensis*.

They are furthermore suitable for controlling the following harmful nematodes, especially plant parasitic nematodes such as root knot nematodes, *Meloidogyne hapla*,
Meloidogyne incognita, *Meloidogyne javanica*, and other *Meloidogyne* species; cyst-
25 forming nematodes, *Globodera rostochiensis* and other *Globodera* species; *Heterodera*
avenae, *Heterodera glycines*, *Heterodera schachtii*, *Heterodera trifolii*, and other
Heterodera species; Seed gall nematodes, *Anguina* species; Stem and foliar
nematodes, *Aphelenchoides* species; Sting nematodes, *Belonolaimus longicaudatus*
and other *Belonolaimus* species; Pine nematodes, *Bursaphelenchus xylophilus* and
30 other *Bursaphelenchus* species; Ring nematodes, *Criconema* species, *Criconemella*
species, *Criconemoides* species, *Mesocriconema* species; Stem and bulb nematodes,
Ditylenchus destructor, *Ditylenchus dipsaci* and other *Ditylenchus* species; Awl
nematodes, *Dolichodorus* species; Spiral nematodes, *Helicotylenchus multicinctus* and
other *Helicotylenchus* species; Sheath and sheathoid nematodes, *Hemicycliophora*
35 species and *Hemicriconemoides* species; *Hirshmanniella* species; Lance nematodes,
Hoploaimus species; false rootknot nematodes, *Nacobbus* species; Needle nematodes,
Longidorus elongatus and other *Longidorus* species; Lesion nematodes, *Pratylenchus*
neglectus, *Pratylenchus penetrans*, *Pratylenchus curvatus*, *Pratylenchus goodeyi* and
other *Pratylenchus* species; Burrowing nematodes, *Radopholus similis* and other

Radopholus species; Reniform nematodes, Rotylenchus robustus and other Rotylenchus species; Scutellonema species; Stubby root nematodes, Trichodorus primitivus and other Trichodorus species, Paratrichodorus species; Stunt nematodes, Tylenchorhynchus claytoni, Tylenchorhynchus dubius and other Tylenchorhynchus species; Citrus nematodes, Tylenchulus species; Dagger nematodes, Xiphinema species; and other plant parasitic nematode species.

In particular, the inventive mixtures are suitable for combating pests of the orders Coleoptera, Lepidoptera, Thysanoptera, Homoptera, Isoptera, and Orthoptera.

They are also suitable for controlling the following plant parasitic nematodes such as Meloidogyne, Globodera, Heterodera, Radopholus, Rotylenchulus, Pratylenchus and other genera.

Suitable targets for seed treatment are various crop seeds, fruit species, vegetables, spices and ornamental seed, for example corn/maize (sweet and field), durum wheat, soybean, wheat, barley, oats, rye, triticale, bananas, rice, cotton, sunflower, potatoes, pasture, alfalfa, grasses, turf, sorghum, rapeseed, Brassica spp., sugar beet, eggplants, tomato, lettuce, iceberg lettuce, pepper, cucumber, squash, melon, bean, dry-beans, peas, leek, garlic, onion, cabbage, carrot, tuber such as sugar cane, tobacco, coffee, turf and forage, cruciferous, cucurbits, grapevines, pepper, fodder beet, oil seed rape, pansy, impatiens, petunia and geranium.

The term seed treatment comprises all suitable seed treatment techniques known in the art, such as, but not limited to, seed dressing, seed coating, seed dusting, seed soaking, seed film coating, seed multilayer coating, seed encrusting, seed dripping, and seed pelleting.

The active ingredient mixtures according to the invention are especially advantageous for seed treatment of oil seed rape, wheat, corn, rye, barley, oats, sorghum, sunflowers, rice, maize, turf and forage, cotton, sugar beet, beans, peas, soybeans, ornamentals, and vegetables such as cucurbits, tomatoes, eggplant, potatoes, pepper, lettuce, cabbage, carrots, cruciferous.

Especially preferred is the seed treatment of oil seed rape, wheat, beans, corn, soybeans, cotton, sorghum, sugar beet, rice, vegetables, and ornamentals.

The mixtures according to the invention are most preferably used for the seed treatment of oil seed rape.

In addition, mixtures according to the invention may also be used in crops which tolerate the action of herbicides or fungicides or insecticides owing to breeding, including genetic engineering methods.

5

For example, mixtures according to the invention can be employed in transgenic crops which are resistant to herbicides from the group consisting of the sulfonylureas, imidazolinones, glufosinate-ammonium or glyphosate-isopropylammonium and analogous active substances (see for example, EP-A 242 236, EP-A 242 246) (WO 92/00377) (EP-A 257 993, US 5,013,659) or in transgenic crop plants, for example cotton, with the capability of producing *Bacillus thuringiensis* toxins (Bt toxins) which make the plants resistant to certain pests (EP-A 142 924, EP-A 193 259).

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Furthermore, mixtures according to the invention can be used also for the treatment of plants which have modified characteristics in comparison with existing plants consist, which can be generated for example by traditional breeding methods and/or the generation of mutants, or by recombinant procedures). For example, a number of cases have been described of recombinant modifications of crop plants for the purpose of modifying the starch synthesized in the plants (e.g. WO 92/11376, WO 92/14827, WO 91/19806) or of transgenic crop plants having a modified fatty acid composition (WO 91/13972).

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The compounds of formula I and II and optionally the further active ingredient(s) 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

The compounds of formula I and II are usually applied in an effective amount, preferably in a weight ratio of from 100:1 to 1:100, more preferably from 100:1 to 1:20, in particular from 20:1 to 1:20, preferably from 10:1 to 1:10.

35

The mixture of compounds of formula I and II and the further active compound III are usually applied in an effective amount, preferably in a weight ratio of from 1000:1 to 1:1000.

Depending on the desired effect, the application rates of the mixtures according to the invention are, especially in the case of areas under agricultural cultivation, from 5 to 2 000 g/ha, preferably from 50 to 1 500 g/ha, in particular from 50 to 750 g/ha.

Here, the application rates of the compound of formula I are from 1 g to 1 kg/ha, preferably from 10 to 900 g/ha, in particular from 20 to 750 g/ha.

Correspondingly, the application rates of the compound of formula II are from 1 g to 1 kg/ha, preferably from 10 to 750 g/ha, in particular from 20 to 500 g/ha.

Correspondingly, the application rates of the further active compound III are from 1 g to 1 kg/ha, preferably from 5 to 900 g/ha, in particular from 10 to 750 g/ha.

In the treatment of seed, the application rates of the mixture according to the invention are generally from 3 kg : 30 g a.i./100 kg, 100 g : 1 g a.i./100 kg, 30 g : 3 kg a.i./100 kg or 1 g : 100g a.i./100 kg. For some specific crop seeds, such as lettuce or onions, the rates can be higher.

A further embodiment of the present invention is directed to the seeds being treated with the mixture according to the present invention.

The novel active ingredient mixtures have very advantageous curative, preventive and systemic fungicidal properties for protecting cultivated plants. As has been mentioned, said active ingredient mixtures can be used to inhibit or destroy the pathogens that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops or useful plants, while at the same time those parts of plants which grow later are also protected from attack by such pathogens. Active ingredient mixtures have the special advantage of being highly active against diseases in the soil that mostly occur in the early stages of plant development.

In the control of phytopathogenic harmful fungi and/or harmful insects and/or nematodes, especially in the control of phytopathogenic harmful fungi and/or harmful insects, the separate or joint application of the compounds of formula I and compounds II and optionally of the further active ingredient or of a mixture according to the invention is carried out by treating the seeds, the plants or the soils before or after sowing of the plants or before or after emergence of the plants.

The active compounds, and the mixtures according to the invention can be prepared, for example, in the form of directly sprayable solutions, powders and suspensions or in the form of highly concentrated aqueous, oily or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, compositions for spreading or granules, and be applied by spraying, atomizing, dusting, broadcasting or watering or colored suspension, solution, emulsion to be applied as such or as water based slurry with seed treatment machinery.

The use form depends on the particular purpose; in each case, it should ensure a distribution of the mixture according to the invention, which is as fine and uniform as possible.

5 The active compounds, and the mixtures can be converted into the customary formulations, for example solutions, emulsions, suspensions, 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 compound according to the invention.

10 The formulations are prepared in a known manner (see e.g. for review 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, pages 8-57 and et seq. 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, 15 US 3,299,566, Klingman, Weed Control as a Science, John Wiley and Sons, Inc., New York, 1961, Hance et al., Weed Control Handbook, 8th Ed., Blackwell Scientific Publications, Oxford, 1989 and Mollet, H., Grubemann, A., Formulation technology, Wiley VCH Verlag GmbH, Weinheim (Germany), 2001, 2. D. A. Knowles, Chemistry and Technology of Agrochemical Formulations, Kluwer Academic Publishers, Dordrecht, 20 1998 (ISBN 0-7514-0443-8), for example by extending the active compound with auxiliaries suitable for the formulation of agrochemicals, such as solvents and/or carriers, if desired emulsifiers, surfactants and dispersants, preservatives, antifoaming agents, anti-freezing agents, for seed treatment formulation also optionally colorants and/or binders and/or gelling agents.

25 Examples of suitable solvents are water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, 30 fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used.

Suitable emulsifiers are nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates).

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Examples of dispersants are lignin-sulfite waste liquors and methylcellulose.

Suitable surfactants used are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid,

dibutyl-naphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and
5 formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenol 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,
10 lignosulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or
15 animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, highly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone or water.

20 Also anti-freezing agents such as glycerin, ethylene glycol, propylene glycol and bactericides such as can be added to the formulation.

Suitable antifoaming agents are for example antifoaming agents based on silicon or magnesium stearate.

25 Suitable preservatives are for example dichlorophenol and enzyalkoholhemiformal.

Seed Treatment formulations may additionally comprise binders and optionally colorants.

30 Binders can be added to improve the adhesion of the active materials on the seeds after treatment. Suitable binders are block copolymers EO/PO surfactants but also polyvinylalcohol, polyvinylpyrrolidones, polyacrylates, polymethacrylates, polybutenes, polyisobutylenes, polystyrene, polyethyleneamines, polyethyleneamides,
35 polyethyleneimines (Lupasol®, Polymine®), polyethers, polyurethanes, polyvinylacetate, tylose and copolymers derived from these polymers.

Optionally, also colorants can be included in the formulation. Suitable colorants or dyes for seed treatment formulations are 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, pigment orange 34, pigment orange 5, pigment green 36, pigment green 7, pigment white 6,
5 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.

An Example of a gelling agent is carrageen (Satiagel®).

10 Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers.

15 Examples of solid 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, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate,
20 ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compound(s). In this case, the active compound(s) are
25 employed in a purity of from 90% to 100% by weight, preferably 95% to 100% by weight(according to NMR spectrum).

For seed treatment purposes, respective formulations can be diluted 2-10 fold leading to concentrations in the ready to use preparations of 0,01 to 60% by weight active
30 compound by weight, preferably 0,1 to 40% by weight.

The compound(s) of formula I, and the mixtures can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions,
35 pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; they are intended to ensure in each case the finest possible distribution of the active compound(s) according to the invention.

Aqueous use 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.

- 5 However, it is also 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.

- 10 The active compound 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 0.01 to 1% per weight.

- 15 The active compound(s) may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

The following are examples of formulations:

- 20 1. Products for dilution with water for foliar applications. For seed treatment purposes, such products may be applied to the seed diluted or undiluted.

A) Water-soluble concentrates (SL, LS)

- 25 10 parts by weight of the active compound(s) are dissolved in 90 parts by weight of water or a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound(s) dissolves upon dilution with water, whereby a formulation with 10 % (w/w) of active compound(s) is obtained.

B) Dispersible concentrates (DC)

- 30 20 parts by weight of the active compound(s) are dissolved in 70 parts by weight of cyclohexanone with addition of 10 parts by weight of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion, whereby a formulation with 20% (w/w) of active compound(s) is obtained.

C) Emulsifiable concentrates (EC)

- 35 15 parts by weight of the active compound(s) are dissolved in 7 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, whereby a formulation with 15% (w/w) of active compound(s) is obtained.

D) Emulsions (EW, EO, ES)

25 parts by weight of the active compound(s) 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 emulsifier machine (e.g. Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion, whereby a formulation with 25% (w/w) of active compound(s) is obtained.

E) Suspensions (SC, OD, FS)

In an agitated ball mill, 20 parts by weight of the active compound(s) are comminuted with addition of 10 parts by weight of dispersants, wetters and 70 parts by weight of water or of an organic solvent to give a fine active compound(s) suspension. Dilution with water gives a stable suspension of the active compound(s), whereby a formulation with 20% (w/w) of active compound(s) is obtained.

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

50 parts by weight of the active compound(s) are ground finely with addition of 50 parts by weight of dispersants and wetters and made as water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound(s), whereby a formulation with 50% (w/w) of active compound(s) is obtained.

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

75 parts by weight of the active compound(s) are ground in a rotor-stator mill with addition of 25 parts by weight of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound(s), whereby a formulation with 75% (w/w) of active compound(s) is obtained.

Gel-Formulation (GF)

In an agitated ball mill, 20 parts by weight of the active compound(s) 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 active compound(s) suspension. Dilution with water gives a stable suspension of the active compound(s), whereby a formulation with 20% (w/w) of active compound(s) is obtained.

2. Products to be applied undiluted for foliar applications. For seed treatment purposes, such products may be applied to the seed diluted.

I) Dustable powders (DP, DS)

5 parts by weight of the active compound(s) are ground finely and mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dustable product having 5% (w/w) of active compound(s)

5

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

0.5 part by weight of the active compound(s) is ground finely and associated with 95.5 parts by weight of carriers, whereby a formulation with 0.5% (w/w) of active compound(s) is obtained. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted for foliar use.

10

K) ULV solutions (UL)

10 parts by weight of the active compound(s) are dissolved in 90 parts by weight of an organic solvent, for example xylene. This gives a product having 10% (w/w) of active compound(s), which is applied undiluted for foliar use.

15

Conventional seed treatment formulations include for example flowable concentrates FS, solutions LS, powders for dry treatment DS, water dispersible powders for slurry treatment WS, water-soluble powders SS and emulsion ES and EC and gel formulation GF. These formulation can be applied to the seed diluted or undiluted. Application to the seeds is carried out before sowing, either directly on the seeds.

20

In a preferred embodiment a FS formulation is used for seed treatment. Typically, a FS formulation may comprise 1-800 g/l of active ingredient, 1-200 g/l Surfactant, 0 to 200 g/l antifreezing agent, 0 to 400 g/l of binder, 0 to 200 g/l of a pigment and up to 1 liter of a solvent, preferably water.

25

The active compound 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 0.01 to 1%.

30

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

35

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 agents according to the invention in a weight ratio of 1:100 to 100:1, preferably 1:10 to 10:1.

Suitable adjuvants in this sense are in particular: organically modified polysiloxanes, for example Break Thru S 240®; alcohol alkoxylates, for example Atplus 245®, Atplus MBA 1303®, Plurafac LF 300® and Lutensol ON 30®; EO/PO block polymers, for example
5 Pluronic RPE 2035® and Genapol B®; alcohol ethoxylates, for example Lutensol XP 80®; and sodium dioctylsulfosuccinate, for example Leophen RA®.

The testing of the mixtures according to the present invention shows that said mixtures are effective in controlling fungi and/or insects and/or nematodes, and improving plant
10 health.

Use examples

The fungicidal effect of the compounds and the mixtures was demonstrated by the
15 following tests:

Preparation: The spray solutions were prepared in several steps:

A stock solution was prepared: a mixture of acetone and/or DMSO and the wetting
20 agent/emulsifier Uniperol, which is based on ethoxylated alkylphenoles, in a relation (volume) solvent-emulsifier of 99 to 1 was added to 25 mg of the compound to give a total of 10 ml. Water was then added to total volume of 100 ml.
This stock solution was diluted with the described solvent-emulsifier-water mixture to the
given concentration.

25 Use Example 1 - Control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*

The first fully developed leaves of pot grown wheat were sprayed to run-off with an
30 aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The next day the treated plants were inoculated with spores of *Blumeria graminis* f. sp. *tritici* (= syn. *Erysiphe graminis* f. sp. *tritici*) by shaking heavily infested stock plants over the treated pots. After cultivation in the greenhouse for 7 days
at 22-26°C and a relative humidity between 60 to 90 % the extent of fungal attack on the
35 leaves was visually assessed as % diseased leaf area.

The visually determined percentages of infected leaf areas were converted into efficacies in % of the untreated control:

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

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

- 5 α corresponds to the fungicidal infection of the treated plants in % and
 β corresponds to the fungicidal infection of the untreated (control) plants in %

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

15 The expected efficacies of active compound combinations were determined using Colby's formula (Colby, S.R. "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds, 15, 20-22, 1967) and compared with the observed efficacies.

Colby's formula:

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

- 20 E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b
 x efficacy, expressed in % of the untreated control, when using the active compound A at the concentration a
 y efficacy, expressed in % of the untreated control, when using the active compound
 25 B at the concentration b

Table 1A – Individual active compounds

No.	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
1	control (untreated)	-	(70% infection)
2	Clothianidine	0.25	0
3	Fluoxastrobin	0.063	0

Table 1B – Mixtures according to the invention of the active compounds from Table 1A

No.	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
4	Clothianidine + Fluofoxastrobin 0.25 + 0.063 ppm 4:1	29	0

Use Example 2 - Control of net blotch on barley caused by *Pyrenophora teres*

5

The first fully developed leaves of pot grown barley plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mentioned in the table below. The next day the treated plants were inoculated with an aqueous spore suspension of *Pyrenophora* (syn. *Drechslera*) *teres*. Then the trial plants were immediately transferred to a humid chamber in the greenhouse. After 6 days of cultivation at 20-24°C and a relative humidity close to 70 %, the extent of fungal attack on the leaves was visually assessed as % leaf area.

10

Evaluation was carried out analogously to example 1.

15

Table 2A – Individual active compounds

No.	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
5	control (untreated)	-	(70% infection)
6	Clothianidine	16	0
7		4	0
8	Fluofoxastrobin	0.25	0

20

25

Table 2B – Mixtures according to the invention of the active compounds from Table 2A

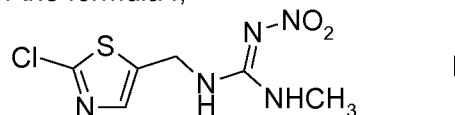
No.	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
9	Clothianidine + Fluoastobin 16 + 0.25 ppm 64:1	71	0
10	Clothianidine + Fluoastobin 4 + 0.25 ppm 16:1	43	0

5 The test results show that, by virtue of the synergism, the mixtures according to the invention are considerably more effective than had been predicted using Colby's formula.

Claims:

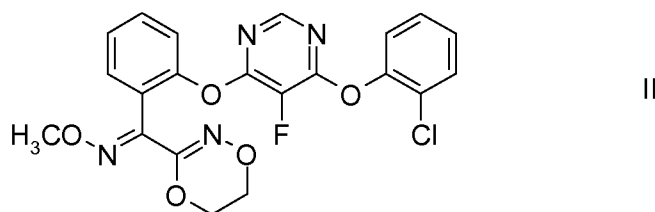
1. Pesticidal mixtures comprising

5 a) clothianidine of the formula I,



and

10 b) fluoxastrobin of the formula II,



in synergistically effective amounts.

15 2. Pesticidal mixture according to claim 1, comprising the compound of the formula I and the compound of the formula II in a weight ratio of from 100:1 to 1:100.

3. Pesticidal mixture according to claim 1 or 2, comprising a further active compound III against harmful fungi or other pests, such as insects, arachnids or nematodes, or herbicidal or growth-regulating active compounds or fertilizers.

20 4. Pesticidal mixtures according to any one of claims 1 to 3, wherein the compound II is selected from the group consisting of carbamates according to claim 1.

25 5. Pesticidal mixtures according to claim 4, wherein the compound II is selected from the group consisting of carbofuran, carbosulfan, and thiodicarb.

6. Pesticidal mixtures according to any one of claims 1 to 3, wherein the compound II is selected from the group consisting of pyrethroids according to claim 1.

30 7. Pesticidal mixtures according to claim 6, wherein the compound II is selected from the group consisting of bifenthrin, cyfluthrin, cypermethrin, alpha-cypermethrin, and tefluthrin.

8. Pesticidal mixtures according to any one of claims 1 to 3, wherein the compound II

is selected from the group consisting of nicotinic receptor agonists/antagonists compounds according to claim 1.

- 5 9. Pesticidal mixtures according to claim 8, wherein the compound II is selected from the group consisting of acetamiprid, clothianidin, dinotefuran, imidacloprid, spinosad, thiamethoxam, and thiacloprid.
- 10 10. Pesticidal mixtures according to claim 8 or 9, wherein the compound II is clothianidin.
- 11 11. Pesticidal mixtures according to any one of claims 1 to 3, wherein the compound II is selected from the group consisting of GABA gated chloride channel antagonist compounds according to claim 1.
- 15 12. Pesticidal mixtures according to claim 11, wherein the compound II is fipronil.
- 20 13. A method of improving the health of plants, which comprises applying in any desired sequence, simultaneously, that is, jointly or separately, or in succession, effective amounts of a mixture as claimed in any one of claims 1 to 12.
- 25 14. A method of controlling or preventing fungal infestation in plants, parts of plants, seeds, or at their locus of growth, which comprises applying in any desired sequence, simultaneously, that is, jointly or separately, or in succession, synergistically effective amounts of a mixture as claimed in any one of claims 1 to 12.
- 30 15. A method of controlling or preventing harmful insects or nematodes in plants, parts of plants, seeds, or at their locus of growth, which comprises applying in any desired sequence, simultaneously, that is, jointly or separately, or in succession, synergistically effective amounts of a mixture as claimed in any one of claims 1 to 12.
- 35 16. A method as claimed in claims 13, 14 or 15, wherein the mixture as claimed in claims 1 to 12 is applied in an amount of from 0.1 g/ha to 2000 g/ha.
17. A method of protection of seeds comprising contacting the seeds before sowing and/or after pregermination with a mixture as defined in claims 1 to 12.
18. A method as claimed in claim 17 wherein the mixture as defined in claims 1 to 12

is applied in an amount of from 0.1 g to 5 kg per 100 kg of seeds.

19. Plant propagation material treated with the mixtures as defined in claims 1 to 12.
- 5 20. The plant propagation material of claim 19, wherein seeds are the propagation material.
21. Seed, comprising the mixture as claimed in claims 1 to 12 in an amount of from 0.1 g to 5 kg per 100 kg of seeds.
- 10 22. Pesticidal composition, comprising a liquid or solid carrier and a mixture according to any of claims 1 to 12.
- 15 23. A process for preparing a composition as claimed in claim 22 by extending the compound of formula I and the compound of formula II with solvents and/or carriers.