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(54) Title: ACTIVE COMPOUND COMBINATIONS

(57) Abstract: The invention relates to active compound combinations, in particular a fungicidal composition, comprising (A), (B) and (C). Moreover, the invention relates to a method for curatively or preventively controlling the phytopathogenic fungi and/or microorganisms and/or pests of plants or crops, to the use of a combination according to the invention for the treatment of seed, to a method for protecting a seed and not at least to the treated seed. X



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Active compound combinations

The invention relates to active compound combinations, in particular a fungicidal composition, comprising (A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate, (B) fosetyl-aluminium (aluminium tris(ethyl phosphonate) and at least one compound selected from the group consisting of (C) Mancozeb or Metiram. Moreover, the invention relates to a method for curatively or preventively controlling the phytopathogenic fungi and/or microorganisms and/or pests of plants or crops, to the use of a combination according to the invention for the treatment of seed, to a method for protecting a seed and not at least to the treated seed.

10 It is already known that the compound 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate has fungicidal properties (CAS No 1360819-11-9, known from WO2012/025557). However, Oomycete diseases are in the focus of the spectrum of activity of this substance.

15 In addition, it has also been found that 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methane-sulfonate in combination with other fungicides gives synergistic combinations for controlling phytopathogenic fungi of plants or crops (WO 2013/127704). However, Oomycete diseases are in the focus of the spectrum of activity of these mixtures.

20 Furthermore, it is already known that phosphonic acid and derivatives (phosphonates) like the phosphonate ethyl hydrogen phosphonate with common name fosetyl-aluminium (CAS No 39148-24-8, known from FR-A-2254276) and its derivatives can be used for controlling phytopathogenic fungi of plant and crops (Pesticide Manual, 14th. Edition (2006); "Modern Agrochemicals", Vol. 4, No. 3, June 2005). However, the activity of these substances at low application rates is not always sufficient.

25 It is also known that the compound Mancozeb (manganese, [N-[2-[(dithiocarboxy)amino]-ethyl]carbamidithioato(2-)-κS,κS']-, mixt. with [N-[2-[(dithiocarboxy)amino]ethyl]carbamidithioato(2-)-κS,κS']zinc, CAS No. 8018-01-7, known from DE1234704 and WO 2010/043319) is also suitable for controlling phytopathogenic fungi of plants and crops. However, the activity of this substance at low application rates is likewise not always sufficient.

30 It is also known that the compound Metiram (zincammoniateethylenebis(dithiocarbamate)-poly(ethylenethiuramdisulfide), CAS No. 9006-42-2, known from DE1076434) is also suitable for controlling phytopathogenic fungi of plants and crops. However, the activity of this substance at low application rates is likewise not always sufficient.

Since, moreover, the environmental and economic requirements imposed on modern-day fungicides are continually increasing, with regard, for example, to the spectrum of action, toxicity, selectivity, application rate, formation of residues, and favorable preparation ability, and since, furthermore, there may be problems, for example, with resistances developing to known active compounds, a constant task is to develop new fungicide agents which in some areas at least have advantages over their known counterparts.

The invention provides active compound combinations which have not only very good fungicidal properties but also shows additive enhancement of the spectrum of action with respect to the phytopathogenic fungi and/or microorganisms and/or pests to be controlled and above all achieves a synergistic effect which extends the range of action of the compound (A), (B) and (C) in two ways. Firstly, the rates of application of the compounds (A), (B) and (C) are lowered whilst the action remains equally good. Secondly, the combination still achieves a high degree of phytopathogen control even where the three individual compounds have become nearly ineffective in such a low application rate range. This allows, on the one hand, a substantial broadening of the spectrum of phytopathogens that can be controlled and, on the other hand, increased safety in use.

However, besides the actual synergistic action with respect to fungicidal activity, the combination according to the invention also have further surprising advantageous properties which can also be described, in a wider sense, as synergistic activity. Examples of such advantageous properties that may be mentioned are: a broadening of the spectrum of fungicidal and/or insecticidal activity to other phytopathogenic fungi and/or microorganisms and/or pests, for example to resistant strains; a reduction in the rate of application of the active ingredients; adequate pest control with the aid of the compositions according to the invention, even at a rate of application at which the individual compounds are totally ineffective; advantageous behavior during formulation or upon application, for example upon grinding, sieving, emulsifying, dissolving or dispensing; increased storage stability; improved stability to light; more advantageous degradability; improved toxicological or ecotoxicological behavior; improved characteristics of the useful plants including: emergence, crop yields, more developed root system, tillering increase, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf color, less fertilizers needed, less seeds needed, more productive tillers, earlier flowering, early grain maturity, less plant verse (lodging), increased shoot growth, improved plant vigor, and early germination; or any other advantages familiar to a person skilled in the art.

Accordingly, the present invention provides an active compound combination comprising:

(A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate and

(B) Fosetyl-aluminium and

(C) at least one compound selected from the group consisting of Mancozeb or Metiram.

In a preferred embodiment the present invention provides an active compound combination comprising:

(A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate and

(B) Fosetyl-aluminium and

(C) Mancozeb.

In a further preferred embodiment the present invention provides an active compound combination comprising:

(A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate and

(B) Fosetyl-aluminium and

(C) Metiram.

The combination according to the invention can also provide an improved systemicity to the active compounds that are used. Indeed, even if some of the used fungicide compound does not possess any or a satisfying systemicity, within the composition according to the invention these compounds can exhibit such a property.

In a similar manner, the combination according to the invention can allow an increased persistence of the fungicide efficacy of the active compounds that are employed.

Another advantage of the combination according to the invention relies in that an increased efficacy is achievable.

In a preferred embodiment the active compound combination according to the present invention is leading to one or more of the following properties: additive enhancement of the spectrum, synergistic effect, improved yields, better developed root system, greener leaves, tillering increase, increased plant height, bigger leaf blade, less dead basal leaves, stronger tillers, less fertilizer needed, more productive tillers, earlier flowering, earlier grain maturity, less plant verse, increased shoot growth, improved plant vigor, earlier germination, improved systemicity, increased persistence of the fungicide efficacy, increased achievable efficacy.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: additive enhancement of the spectrum.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: synergistic effect.

- 5 Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: improved yield.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: better developed root system.

- 10 Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: greener leaves.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: tillering increase.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: increased plant height.

- 15 Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: bigger leaf blade.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: less dead basal leaves.

- 20 Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: stronger tillers.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: less fertilizer needed.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: more productive tillers.

- 25 Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: earlier flowering.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: earlier grain maturity.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: less plant verse.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: increased shoot growth.

- 5 Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: earlier germination.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: improved plant vigor.

- 10 Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: improved systemicity.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: increased persistence of the fungicide efficacy.

Furthermore preferred is that the active compound combination according to the present invention is leading to the following property: increased achievable efficacy.

- 15 For the ternary mixtures the weight ratio of active ingredient compounds is selected as to give the desired, for example synergistic, action:

In preferred embodiments of the invention the weight ratio of A:B is from 1:500 to 1:50, preferably from 1:200 to 1:100, more preferably from 1:200 to 1:150.

- 20 In preferred embodiments of the invention the weight ratio of A:C is from 1:500 to 1:50, preferably from 1:300 to 1:100, more preferably from 1:140 to 1:170, if C is Mancozeb.

In preferred embodiments of the invention the weight ratio of A:C is from 1:500 to 1:50, preferably from 1:300 to 1:100, more preferably from 1:130 to 1:160, if C is Metriam.

In preferred embodiments of the invention the weight ratio of B:C is from 10:1 to 1:10, preferably from 2:3 to 1:1, more preferably from 2:1 to 1:1, if C is Mancozeb.

- 25 In preferred embodiments of the invention the weight ratio of B:C is from 10:1 to 1:10, preferably from 2:3 to 1:1, more preferably from 2:1 to 1:1, if C is Metriam.

In preferred embodiments of the invention the weight ratio of A:B is from from 1:500 to 1:50 and the weight ratio of A:C is from 1:500 to 1:50, preferably the weight ratio of A:B is from 1:200 to 1:100 and

the weight ratio of A:C is from 1:300 to 1:100, more preferably the weight ratio of A:B is from 1:200 to 1:150 and the weight ratio of A:C is from 1:140 to 1:170, if C is Mancozeb.

In preferred embodiments of the invention the weight ratio of A:B is from 1:500 to 1:50 and the weight ratio of B:C is from 10:1 to 1:10, preferably the weight ratio of A:B is from 1:200 to 1:100 and the weight ratio of B:C is from 2:3 to 1:1, more preferably the weight ratio of A:B is from 1:200 to 1:150 and the weight ratio of B:C is from 2:1 to 1:1, if C is Mancozeb.

In preferred embodiments of the invention the weight ratio of A:C is from 1:500 to 1:50 and the weight ratio of B:C is from 10:1 to 1:10, preferably the weight ratio of A:C is from 1:300 to 1:100 and the weight ratio of B:C is from 2:3 to 1:1, more preferably the weight ratio of A:C is from 1:140 to 1:170, and the weight ratio of B:C is from 2:1 to 1:1, if C is Mancozeb.

In preferred embodiments of the invention the weight ratio of A:B is from 1:500 to 1:50, the weight ratio of A:C is from 1:500 to 1:50 and the weight ratio of B:C is from 10:1 to 1:10, preferably the weight ratio of A:B is from 1:200 to 1:100, the weight ratio of A:C is from 1:300 to 1:100 and the weight ratio of B:C is from 2:3 to 1:1, more preferably the weight ratio of A:B is from 1:200 to 1:150, the weight ratio of A:C is from 1:140 to 1:170 and the weight ratio of B:C is from 2:1 to 1:1, if C is Mancozeb.

In preferred embodiments of the invention the weight ratio of A:B is from 1:500 to 1:50 and the weight ratio of A:C is from 1:500 to 1:50, preferably the weight ratio of A:B is from 1:200 to 1:100 and the weight ratio of A:C is from 1:300 to 1:100, more preferably the weight ratio of A:B is from 1:200 to 1:150 and the weight ratio of A:C is from 1:130 to 1:160, if C is Metiram.

In preferred embodiments of the invention the weight ratio of A:B is from 1:500 to 1:50 and the weight ratio of B:C is from 10:1 to 1:10, preferably the weight ratio of A:B is from 1:200 to 1:100 and the weight ratio of B:C is from 2:3 to 1:1, more preferably the weight ratio of A:B is from 1:200 to 1:150 and the weight ratio of B:C is from 2:1 to 1:1, if C is Metiram.

In preferred embodiments of the invention the weight ratio of A:C is from 1:500 to 1:50 and the weight ratio of B:C is from 10:1 to 1:10, preferably the weight ratio of A:C is from 1:300 to 1:100 and the weight ratio of B:C is from 2:3 to 1:1, more preferably the weight ratio of A:C is from 1:130 to 1:160 and the weight ratio of B:C is from 2:1 to 1:1, if C is Metiram.

In preferred embodiments of the invention the weight ratio of A:B is from 1:500 to 1:50, the weight ratio of A:C is from 1:500 to 1:50 and the weight ratio of B:C is from 10:1 to 1:10, preferably the weight ratio of A:B is from 1:200 to 1:100, the weight ratio of A:C is from 1:300 to 1:100 and the weight ratio of B:C is from 2:3 to 1:1, more preferably the weight ratio of A:B is from 1:200 to 1:150,

the weight ratio of A:C is from 1:130 to 1:160 and the weight ratio of B:C is from 2:1 to 1:1, if C is Metiram.

The weight ratio for ternary mixtures (A):(B):(C) is 1:500:500 to 1:50:50; more preferred (A):(B):(C) is 1:200:300 to 1:100:100; most preferred is (A):(B):(C) is 1:200:160 if (C) is Mancozeb; furthermore
5 preferred is (A):(B):(C) is 1:200:150 if (C) is Metiram.

Where a compound (A), (B) or (C) can be present in tautomeric form, such a compound is understood hereinabove and herein below also to include, where applicable, corresponding tautomeric forms, even when these are not specifically mentioned in each case.

Compound (A), (B) or (C) having at least one basic centre are capable of forming, for example, acid
10 addition salts, e.g. with strong inorganic acids, such as mineral acids, e.g. perchloric acid, sulfuric acid, nitric acid, nitrous acid, a phosphoric acid or a hydrohalic acid, with strong organic carboxylic acids, such as unsubstituted substituted, e.g. halo-substituted, C₁-C₄ alkanecarboxylic acids, e.g. acetic acid, saturated or unsaturated dicarboxylic acids, e.g. oxalic, malonic, succinic, maleic, fumaric and phthalic acid, hydroxycarboxylic acids, e.g. ascorbic, lactic, malic, tartaric and citric acid, or benzoic acid, or
15 with organic sulfonic acids, such as unsubstituted or substituted, e.g. halo-substituted, C₁-C₄ alkane- or aryl-sulfonic acids, e.g. methane- or p-toluene-sulfonic acid. Compounds (A) or compound (B) having at least one acid group are capable of forming, for example, salts with bases, e.g. metal salts, such as alkali metal or alkaline earth metal salts, e.g. sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkylamine, e.g.
20 ethyl-, diethyl-, triethyl- or dimethyl-propyl-amine, or a mono-, di- or tri-hydroxy-lower alkylamine, e.g. mono-, di- or tri-ethanolamine. In addition, corresponding internal salts may optionally be formed. In the context of the invention, preference is given to agrochemically advantageous salts. In view of the close relationship between the compound (A), (B) or (C) in free form and in the form of their salts, hereinabove and herein below any reference to the free compound (A), (B) or (C) or to their salts should
25 be understood as including also the corresponding salts or the free compound (A), (B) or (C), respectively, where appropriate and expedient. The equivalent also applies to tautomers of compound (A), (B) or (C) and to their salts.

According to the invention the expression "combination" stands for the various combinations of compounds (A) and (B) and (C), for example in a single "ready-mix" form, in a combined spray mixture
30 composed from separate formulations of the single active compounds, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. Preferably the order of applying the compounds (A) and (B) and (C) is not essential for working the present invention.

According to the invention the expression "pathogen" stands for all organisms which cause damages on plants or any part of a plant.

According to the invention the expression "fungi" stands for all fungal and chromista organisms.

5 According to the invention the expression "phytopathogenic fungi" stands for all fungal and chromista organisms which cause damages on plants or any part of a plant. Examples for fungal taxonomic groups are Ascomycota, Basidiomycota, Chytridiomycota, Deuteromycota, Glomeromycota, Microsporidia, Zygomycota, and anamorphic fungi. Examples for Chromista are Oomycota.

According to the invention the expression "microorganisms" stands for all bacterial and protozoan organisms. Examples are Plasmodiophoromycetes.

10 The active compounds within the composition according to the invention have potent microbicide activity and can be employed for controlling undesired phytopathogenic fungi and/or microorganisms and/or pests, in crop protection or in the protection of materials.

Within the composition according to the invention, fungicide compounds can be employed in crop protection for example for controlling phytopathogenic fungi and/or microorganisms such as
15 Plasmodiophoromycetes, Oomycota, Chytridiomycota, Zygomycota, Ascomycota, Basidiomycota and Deuteromycota.

Within the composition according to the invention, bactericide compounds can be employed in crop protection for controlling microorganisms for example Pseudomonadaceae, Rhizobiaceae, Enterobacteriaceae, Corynebacteriaceae and Streptomycetaceae.

20 Within the composition according to the invention, insecticide compounds can be employed in crop protection for example for controlling pests such as lepidoptera.

The fungicidal combination and/or composition according to the invention can be used to curatively or preventively control the phytopathogenic fungi and/or microorganisms and/or pests of plants or crops. Thus, according to a further aspect of the invention, there is provided a method for curatively or preventively
25 controlling the phytopathogenic fungi and/or microorganisms and/or pests of plants or crops comprising the use of a fungicide composition according to the invention by application to the seed, the plant or to the fruit of the plant or to the soil in which the plant is growing or in which it is desired to grow.

According to the invention all plants and plant parts can be treated. By plants is meant all plants and plant populations such as desirable and undesirable wild plants, cultivars (including naturally occurring
30 cultivars) and plant varieties (whether or not protectable by plant variety or plant breeder's rights).

Cultivars and plant varieties can be plants obtained by conventional propagation and breeding methods which can be assisted or supplemented by one or more biotechnological methods such as by use of double haploids, protoplast fusion, random and directed mutagenesis, molecular or genetic markers or by bioengineering and genetic engineering methods including transgenic plants.

- 5 By plant parts is meant all above ground and below ground parts and organs of plants such as shoot, leaf, flower, blossom and root, whereby for example leaves, needles, stems, branches, blossoms, fruiting bodies, fruits and seed as well as roots, corms and rhizomes are listed. Crops and vegetative and generative propagating material, for example cuttings, corms, rhizomes, runners and seeds also belong to plant parts.
- 10 According to the invention the expression “plant propagation material” stands for all plant material which can be used either in the vegetative or generative reproduction of plants. Examples for plant propagation material are cuttings, corms, rhizomes, runners, seeds, fruits, grains, pods, fruiting bodies, tubers and seedlings.

- The combination/composition according to the invention for combating phytopathogenic fungi and/or
- 15 microorganisms and/or pests in crop protection comprises an effective, but not phytotoxic amount of the active compounds according to the invention. “Effective, but not phytotoxic amount” is defined as an amount of the combination according to the invention which is sufficient on one hand to control satisfactorily or completely eliminate the fungal disease of the plant and which on the other hand does not lead to any noteworthy symptoms of phytotoxicity. The effective dose can be varied in general in a
 - 20 larger range. The dose is dependent on several factors eg the fungi to be combatted, the plant, the climatic conditions, and on the active compounds of the combination according to the invention.

- Among the plants that can be protected by the method according to the invention, mention may be made of major field crops like corn, soybean, cotton, Brassica oilseeds such as Brassica napus (e.g. canola), Brassica
- 25 rapa, B. juncea (e.g. mustard) and Brassica carinata, rice, wheat, sugarbeet, sugarcane, oats, rye, barley, millet, triticale, flax, vine and various fruits and vegetables of various botanical taxa such as *Rosaceae* sp. (for instance pip fruit such as apples and pears, but also stone fruit such as apricots, cherries, almonds and peaches, berry fruits such as strawberries), *Ribesiodae* sp., *Juglandaceae* sp., *Betulaceae* sp., *Anacardiaceae* sp., *Fagaceae* sp., *Moraceae* sp., *Oleaceae* sp., *Actinidaceae* sp., *Lauraceae* sp., *Musaceae* sp. (for instance banana trees and plantings), *Rubiaceae* sp. (for instance coffee), *Theaceae* sp., *Sterculiaceae* sp., *Rutaceae* sp.
 - 30 (for instance lemons, oranges and grapefruit) ; *Solanaceae* sp. (for instance tomatoes, potatoes, peppers, eggplant), *Liliaceae* sp., *Compositiae* sp. (for instance lettuce, artichoke and chicory - including root chicory, endive or common chicory), *Umbelliferae* sp. (for instance carrot, parsley, celery and celeriac), *Cucurbitaceae* sp. (for instance cucumber – including pickling cucumber, squash, watermelon, gourds and melons), *Alliaceae* sp. (for instance onions and leek), *Cruciferae* sp. (for instance white cabbage, red cabbage,

broccoli, cauliflower, brussel sprouts, pak choi, kohlrabi, radish, horseradish, cress, Chinese cabbage, colza), *Leguminosae sp.* (for instance peanuts, peas and beans - such as climbing beans and broad beans), *Chenopodiaceae sp.* (for instance mangold, spinach beet, spinach, beetroots), *Asteraceae sp.* (for instance sunflower), *Brassicaceae sp.* (for instance white cabbage, red cabbage, brokkoli, cauliflower, brussel sprouts, pak choi, kohlrabi, radish as well as canola, rapeseed, mustard, horseradish, cress), *Fabaceae sp.* (for instance peanuts and beans), *Papilionaceae sp.* (for instance soybean), *Solanaceae sp.* (for instance potatoes), *Malvaceae* (for instance okra), *Asparagaceae* (for instance asparagus) ; horticultural and forest crops; ornamental plants ; as well as genetically modified homologues of these crops.

10 Preferebly vine, tobacco, *Solanaceae sp.* (for instance tomatoes, potatoes, eggplant) can be protected by the method according to the invention.

Most preferebly vine can be protected by the method according to the invention.

Most preferebly potatoes can be protected by the method according to the invention.

15 In a very particular embodiment a method for curatively or preventively controlling the phytopathogenic fungi and/or microorganisms and/or pests of plants or crops is described comprising the use of the combination of (A) and (B) and (C) by application to the seed, plant propagation material, the plant or to the fruit of genetically modified plants wherein the active principle expressed by the genetically modified plant corresponds to a line of table A or B.

20 At certain application rates, the active compound combinations according to the invention may also have a strengthening effect in plants. Accordingly, they are also suitable for mobilizing the defense system of the plant against attack by unwanted phytopathogenic fungi and/ or microorganisms and/or viruses. This may, if appropriate, be one of the reasons of the enhanced activity of the combinations according to the invention, for example against fungi. Plant-strengthening (resistance-inducing) substances are to be understood as meaning, in the present context, those substances or combinations of substances which are capable of stimulating the defense system of plants in such a way that, when subsequently inoculated with unwanted
25 phytopathogenic fungi and/or microorganisms and/or pests and/or viruses, the treated plants display a substantial degree of resistance to these phytopathogenic fungi and/or microorganisms and/or pests and/or viruses, Thus, the substances according to the invention can be employed for protecting plants against attack by the abovementioned pathogens within a certain period of time after the treatment. The period of time within which protection is effected generally extends from 1 to 10 days, preferably 1 to 7 days, after
30 the treatment of the plants with the active compounds.

In a further aspect there is provided a composition comprising a combination according to this invention. Preferably the fungicidal and/or insecticidal composition comprises agriculturally acceptable additives, solvents, carriers, surfactants, or extenders.

5 According to the invention, the term “carrier” denotes a natural or synthetic, organic or inorganic compound with which the active combinations (A), (B), (C) are combined or associated to make it easier to apply, notably to the parts of the plant. This support is thus preferably inert and should be at least agriculturally acceptable. The support may be a solid or a liquid.

Suitable solid carriers are the following:

10 e.g. ammonium salts and natural rock powders, such as kaolins, clays, talcum, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth and synthetic rock powders such as highly disperse silica, aluminium oxide and silicates, oil waxes, solid fertilizers, water, alcohols, preferably butanol, organic solvents, mineral and vegetable oils and derivatives thereof;

15 suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite, dolomite and synthetic granules of inorganic and organic powders and granules of organic materials such as paper, sawdust, coconut shells, corn stalks and tobacco stalks;

By liquefied gaseous diluents or supports are meant such liquids that are gaseous at normal temperature and under normal pressure, for example, aerosol propellants such as halohydrocarbons as well as butane, propane, nitrogen and carbon dioxide.

20 It is possible to use in the formulations adhesives such as carboxymethylcellulose, natural and synthetic powdered, granular or latex-like polymers such as gum arabic, polyvinyl alcohol, polyvinyl acetate and natural phospholipids, such as cephalins and lecithins and synthetic phospholipids. Further additives can be mineral or vegetable oils and waxes, optionally modified.

25 Suitable extenders are, for example, water, polar and non-polar organic chemical liquids, for example from the classes of the aromatic and non-aromatic hydrocarbons (such as paraffins, alkylbenzenes, alkylnaphthalenes, chlorobenzenes), the alcohols and polyols (which, if appropriate, may also be substituted, etherified and/or esterified), the ketones (such as acetone, cyclohexanone), esters (including fats and oils) and (poly)ethers, the unsubstituted and substituted amines, amides, lactams (such as *N*-alkylpyrrolidones) and lactones, the sulphones and sulfoxides (such as dimethyl sulphoxide).

30 If the extender used is water, it is also possible to employ, for example, organic solvents as auxiliary solvents. Essentially, suitable liquid solvents are: aromatics such as xylene, toluene or alkyl-naphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or

methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example petroleum fractions, mineral and vegetable oils, alcohols such as butanol or glycol and also their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethyl sulphoxide, and also water.

- 5 The composition according to the invention may also comprise additional components. In particular, the composition may further comprise a surfactant. The surfactant can be an emulsifier, a dispersing agent or a wetting agent of ionic or non-ionic type or a mixture of such surfactants. Mention may be made, for example, of polyacrylic acid salts, lignosulphonic acid salts, phenolsulphonic or naphthalenesulphonic acid salts, polycondensates of ethylene oxide with fatty alcohols or with fatty acids or with fatty amines, 10 substituted phenols (in particular alkylphenols or arylphenols), salts of sulphosuccinic acid esters, taurine derivatives (in particular alkyl taurates), phosphoric esters of polyoxyethylated alcohols or phenols, fatty acid esters of polyols, and derivatives of the present compounds containing sulphate, sulphonate and phosphate functions, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates, protein hydrolyzates, lignosulphite waste liquors and methyl cellulose. The 15 presence of at least one surfactant is generally essential when the active compound and / or the inert support are water-insoluble and when the vector agent for the application is water. Preferably, surfactant content may be comprised from 5% to 40% by weight of the composition.

- Suitable emulsifiers and/or foam-forming agents are: for example non-ionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, suitable dispersants are 20 non-ionic and/or ionic substances, for example from the classes comprising alcohol POE and/or POP ethers, acid and/or POP or POE esters, alkyl-aryl and/or POP or POE ethers, fatty and/or POP-POE adducts, POE and/or POP polyol derivatives, POE and/or POP/sorbitan or sugar adducts, alkyl or aryl sulphates, sulphonates and phosphates or the corresponding PO ether adducts. Furthermore, suitable oligomers or polymers, for example based on vinyl monomers, acrylic acid, EO and/or PO alone or in 25 combination with for example (poly-)alcohols or (poly-)amines. Use can also be made of lignin and sulphonic acid derivatives thereof, simple and modified celluloses, aromatic and/or aliphatic sulphonic acids and adducts thereof with formaldehyde. Suitable as dispersants are for example lignosulphite waste liquors and methylcellulose.

- 30 Colouring agents such as inorganic pigments, for example iron oxide, titanium oxide, ferrocyanblue, and organic pigments such as alizarin, azo and metallophthalocyanine dyes, and trace elements such as iron, manganese, boron, copper, cobalt, molybdenum and zinc salts can be used.

Optionally, other additional components may also be included, e.g. protective colloids, adhesives, thickeners, thixotropic agents, penetration agents, stabilisers, sequestering agents. More generally, the

active compounds can be combined with any solid or liquid additive, which complies with the usual formulation techniques.

In general, the composition according to the invention may contain from 0.05 to 99% by weight of active compounds, preferably from 1 to 70% by weight, most preferably from 10 to 50 % by weight.

- 5 The combination or composition according to the invention can be used as such, in form of their formulations or as the use forms prepared there from, such as aerosol dispenser, capsule suspension, cold fogging concentrate, hot fogging concentrate, encapsulated granule, fine granule, flowable concentrate for seed treatment, ready-to-use solutions, dustable powder, emulsifiable concentrate, emulsion oil in water, emulsion water in oil, macrogranule, microgranule, oil dispersible powder, oil
10 miscible flowable concentrate, oil miscible liquid, froths, paste, seed coated with a pesticide, suspension concentrate (flowable concentrate), suspensions-emulsions-concentrates, soluble concentrate, suspensions, soluble powder, granule, water soluble granules or tablets, water soluble powder for seed treatment, wettable powder, natural and synthetic materials impregnated with active compound, micro-encapsulation in polymeric materials and in jackets for seed, as well as ULV- cold and hot fogging
15 formulations, gas (under pressure), gas generating product, plant rodlet, powder for dry seed treatment, solution for seed treatment, ultra low volume (ULV) liquid, ultra low volume (ULV) suspension, water dispersible granules or tablets, water dispersible powder for slurry treatment.

- These formulations are prepared in a known manner by mixing the active compounds or active compound combinations with customary additives, such as, for example, customary extenders and also
20 solvents or diluents, emulsifiers, dispersants, and/or bonding or fixing agent, wetting agents, water repellents, if appropriate siccatives and UV stabilisers, colorants, pigments, defoamers, preservatives, secondary thickeners, adhesives, gibberellins and water as well further processing auxiliaries.

- These compositions include not only compositions which are ready to be applied to the plant or seed to be treated by means of a suitable device, such as a spraying or dusting device, but also concentrated
25 commercial compositions which must be diluted before application to the crop.

- The control of phytopathogenic fungi and/or microorganisms and/or pests which damage plants post-emergence is carried out primarily by treating the soil and the above-ground parts of plants with crop protection agents. Owing to the concerns regarding a possible impact of crop protection agents on the environment and the health of humans and animals, there are efforts to reduce the amount of active
30 compounds applied.

The active compound combinations according to the invention can be used in its commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active

compounds, such as insecticides, attractants, sterilizing agents, bactericides, acaricides, nematocides, fungicides, growth-regulating substances, herbicides, safeners, fertilizers or semiochemicals.

The treatment of plants and plant parts with the active compound combination according to the invention is carried out directly or by action on their environment, habitat or storage area by means of the normal treatment methods, for example by watering (drenching), drip irrigation, spraying, vaporizing, atomizing, broadcasting, dusting, foaming, spreading-on, and as a powder for dry seed treatment, a solution for seed treatment, a water-soluble powder for seed treatment, a water-soluble powder for slurry treatment, or by encrusting, in the case of propagation material, in particular in the case of seeds, furthermore by dry treatments, slurry treatments, liquid treatments, by one- or multi-layer coating.. It is furthermore possible to apply the active compounds by the ultra-low volume method, or to inject the active compound preparation or the active compound itself into the soil.

The method of treatment according to the invention also provides the use of compounds (A) and (B) and (C) in a simultaneous, separate or sequential manner.

The dose of active compound/ application rate usually applied in the method of treatment according to the invention is generally and advantageously

- for foliar treatments: from 0.1 to 10,000 g/ha, preferably from 100 to 2,000 g/ha, more preferably from 120 to 1500g/ha; in case of drench or drip application, the dose can even be reduced, especially while using inert substrates like rockwool or pelite;
- for seed treatment: from 2 to 200 g per 100 kilogram of seed, preferably from 3 to 150 g per 100 kilogram of seed;
- for soil treatment: from 0.1 to 10,000 g/ha, preferably from 1 to 5,000 g/ha.

The doses herein indicated are given as illustrative examples of the method according to the invention. A person skilled in the art will know how to adapt the application doses, notably according to the nature of the plant or crop to be treated.

The combination according to the invention can be used in order to protect plants within a certain time range after the treatment against pests and/or phytopathogenic fungi and/or microorganisms. The time range, in which protection is effected, spans in general one to 28 days, preferably one to 14 days after the treatment of the plants with the combinations or up to 200 days after the treatment of plant propagation material.

The method of treatment according to the invention may also be useful to treat propagation material such as tubers or rhizomes, but also seeds, seedlings or seedlings pricking out and plants or plants

pricking out. This method of treatment can also be useful to treat roots. The method of treatment according to the invention can also be useful to treat the over-ground parts of the plant such as trunks, stems or stalks, leaves, flowers and fruit of the concerned plant.

5 A further aspect of the present invention is a method of protecting natural substances of vegetable or animal origin or their processed forms, which have been taken from the natural life cycle, which comprises applying to said natural substances of vegetable or animal origin or their processed forms a combination of compounds (A), (B) and (C) in a synergistically effective amount.

The invention comprises a procedure in which the seed is treated at the same time with a compound (A) and (B) and (C). It further comprises a method in which the seed is treated with compound (A) and (B) 10 and (C) separately.

The invention also comprises a seed, which has been treated with a compound (A) and (B) and (C) at the same time. The invention also comprises a seed, which has been treated with a compound (A) and (B) and (C) separately. For the latter seed, the active ingredients can be applied in separate layers. These layers can optionally be separated by an additional layer that may or may not contain an active 15 ingredient.

The combinations and/or compositions of the invention are particularly suitable for the treatment of seeds. A large part of the damage caused by pests and/or phytopathogenic fungi and/or microorganisms on cultigens occurs by infestation of the seed during storage and after sowing the seed in the ground as well as during and after germination of the plants. This phase is especially critical since the roots and 20 shoots of the growing plant are particularly sensitive and even a small amount of damage can lead to withering of the whole plant. There is therefore considerable interest in protecting the seed and the germinating plant by the use of suitable agents.

The control of pests and/or phytopathogenic fungi and/or microorganisms by treatment of the seeds of plants has been known for a considerable time and is the object of continuous improvement. However, 25 there are a number of problems in the treatment of seed that cannot always be satisfactorily solved. Therefore it is worthwhile to develop methods for the protection of seeds and germinating plants which makes the additional application of plant protection agents after seeding or after germination of the plants unnecessary. It is further worthwhile to optimize the amount of the applied active material such that the seed and the germinating plants are protected against infestation by pests and/or 30 phytopathogenic fungi and/or microorganisms as best as possible without the plants themselves being damaged by the active compound applied. In particular, methods for the treatment seed should also take into account the intrinsic fungicidal and/or insecticidal properties of transgenic plants in order to achieve

optimal protection of the seed and germinating plants with a minimal expenditure of plant protection agents.

The present invention relates therefore especially to a method for the protection of seed and germinating plants from infestation with pests and/or phytopathogenic fungi and/or microorganisms in that the seed is treated with the combination/composition of the invention. In addition the invention relates also to the use of the combination/composition of the invention for the treatment seed for protection of the seed and the germinating plants from pests and/or phytopathogenic fungi and/or microorganisms. Furthermore the invention relates to seed which was treated with a combination/ composition of the invention for protection from pests and/or phytopathogenic fungi and/or microorganisms.

One of the advantages of the invention is because of the special systemic properties of the combination/composition of the invention treatment with this combination/ composition protect not only the seed itself from pests and/or phytopathogenic fungi and/or microorganisms but also the plants emerging after sprouting. In this way the direct treatment of the culture at the time of sowing or shortly thereafter can be omitted.

A further advantage is the synergistic increase in fungicidal and/or insecticidal activity of the combination/composition of the invention in comparison to the respective individual active compounds, which extends beyond the sum of the activity of both individually applied active compounds. In this way an optimization of the amount of active compound applied is made possible.

It is also be regarded as advantageous that the mixtures of the invention can also be used in particular with transgenic seeds whereby the plants emerging from this seed are capable of the expression of a protein directed against pests and/or phytopathogenic fungi and/or microorganisms. By treatment of such seed with the agents of the invention certain pests and/or phytopathogenic fungi and/or microorganisms can already be controlled by expression of the, for example, insecticidal protein, and it is additionally surprising that a synergistic activity supplementation occurs with the agents of the invention, which improves still further the effectiveness of the protection from pest infestation.

The agents of the invention are suitable for the protection of seed of plant varieties of all types as already described which are used in agriculture, in greenhouses, in forestry, in furrow treatment, in horticulture or in vineyards. In particular, this concerns seed of cereals (like wheat, barley, rye, triticale, millet, oats, rice), maize, cotton, soya bean, potato, sunflower, beans, coffee, beet (e.g. sugar beet, mangold and feed beet), peanut, canola, rapeseed, poppy, olive, coconut, cacao, sugar cane or tobacco. The combination/ compositions of the invention are also suitable for the treatment of the seed of fruit plants and vegetables (like tomato, cucumber, onion and lettuce), lawn, turf and ornamental plants as

previously described. Particular importance is attached to the treatment of the seed of wheat, barley, rye, triticale, oats, maize, rice, soya bean, cotton, canola, rapeseed.

As already described, the treatment of transgenic seed with a combination/ composition of the invention is of particular importance. This concerns the seeds of plants which generally contain at least one heterologous gene that controls the expression of a polypeptide with special insecticidal properties. The heterologous gene in transgenic seed can originate from microorganisms such as *Bacillus*, *Rhizobium*, *Pseudomonas*, *Serratia*, *Trichoderma*, *Clavibacter*, *Glomus* or *Gliocladium*. The present invention is particularly suitable for the treatment of transgenic seed that contains at least one heterologous gene that originates from *Bacillus sp.* and whose gene product exhibits activity against the European corn borer and/or western corn rootworm. Particularly preferred is a heterologous gene that originates from *Bacillus thuringiensis*.

Within the context of the present invention the combination/composition of the invention is applied to the seed alone or in a suitable formulation. Preferably the seed is handled in a state in which it is so stable, that no damage occurs during treatment. In general treatment of the seed can be carried out at any time between harvest and sowing. Normally seed is used that was separated from the plant and has been freed of spadix, husks, stalks, pods, wool or fruit flesh. Use of seed that was harvested, purified, and dried to moisture content of below 15 % w/w. Alternatively, seed treated with water after drying and then dried again can also be used.

In general care must be taken during the treatment of the seed that the amount of the combination/composition of the invention and/or further additive applied to the seed is so chosen that the germination of the seed is not impaired and the emerging plant is not damaged. This is to be noted above all with active compounds which can show phytotoxic effects when applied in certain amounts.

The combination/ compositions of the invention can be applied directly, that is without containing additional components and without being diluted. It is normally preferred to apply the combination/ composition to the seed in the form of a suitable formulation. Suitable formulations and methods for seed treatment are known to the person skilled in the art and are described, for example, in the following documents: US 4,272,417 A, US 4,245,432 A, US 4,808,430 A, US 5,876,739 A, US 2003/0176428 A1, WO 2002/080675 A1, WO 2002/028186 A2.

The active compound combinations and compositions which can be used according to the invention can be converted into customary seed dressing formulations, such as solutions, emulsions, suspensions, powders, foams, slurries or other coating materials for seed, and also ULV formulations.

These formulations are prepared in a known manner by mixing the active compounds or active compound combinations with customary additives, such as, for example, customary extenders and also solvents or diluents, colorants, wetting agents, dispersants, emulsifiers, defoamers, preservatives, secondary thickeners, adhesives, gibberellins and optionally water as well.

- 5 Suitable colorants that may be present in the seed dressing formulations of the invention include all colorants customary for such purposes. Use may be made both of pigments, of sparing solubility in water, and of dyes, which are soluble in water. Examples that may be mentioned include the colorants known under the designations rhodamine B, C.I. Pigment Red 112, and C.I. Solvent Red 1.

- 10 Suitable wetting agents that may be present in the seed dressing formulations of the invention include all substances which promote wetting and are customary in the formulation of active agrochemical substances. With preference it is possible to use alkyl-naphthalene-sulphonates, such as diisopropyl- or diisobutyl-naphthalene-sulphonates.

- 15 Suitable dispersants and/or emulsifiers that may be present in the seed dressing formulations of the invention include all nonionic, anionic, and cationic dispersants which are customary in the formulation of active agrochemical substances as outlined above.

Suitable defoamers that may be present in the seed dressing formulations of the invention include all foam-inhibiting substances which are customary in the formulation of active agrochemical substances. With preference it is possible to use silicone defoamers and magnesium stearate.

- 20 Suitable preservatives that may be present in the seed dressing formulations of the invention include all substances which can be used for such purposes in agrochemical compositions. By way of example, mention may be made of dichlorophen and benzyl alcohol hemiformal.

- 25 Suitable secondary thickeners that may be present in the seed dressing formulations of the invention include all substances which can be used for such purposes in agrochemical compositions. Preferred suitability is possessed by cellulose derivatives, acrylic acid derivatives, xanthan, modified clays, and highly disperse silica.

Suitable adhesives that may be present in the seed dressing formulations of the invention include all customary binders which can be used in seed dressing. With preference, mention may be made of polyvinylpyrrolidone, polyvinyl acetate, polyvinyl alcohol and tylose.

- 30 Suitable gibberellins that may be present in the seed dressing formulations of the invention include preferably gibberelin A1, A3 (=gibberellinic acid), A4, and A7, particular preferably gibberelin A3 (=gibberellinic acid). The gibberellins of the formula (II) are known, the nomenclature of the gibberellins

can be found the reference mentioned below (cf. R. Wegler "Chemie der Pflanzenschutz- and Schädlingsbekämpfungsmittel", Volume 2, Springer Verlag, Berlin-Heidelberg-New York, 1970, pages 401 - 412).

5 Sutable mixing equipment for treating seed with the seed dressing formulations to be used according to the invention or the preparations prepared from them by adding water includes all mixing equipment which can commonly be used for dressing. The specific procedure adopted when dressing comprises introducing the seed into a mixer, adding the particular desired amount of seed dressing formulation, either as it is or following dilution with water beforehand, and carrying out mixing until the formulation is uniformly distributed on the seed. Optionally, a drying operation follows.

10 Among the diseases of plants or crops that can be controlled by the method according to the invention, mention may be made of :

diseases caused by powdery mildew pathogens, for example *Blumeria* species, for example *Blumeria graminis*; *Podosphaera* species, for example *Podosphaera leucotricha*; *Sphaerotheca* species, for example *Sphaerotheca fuliginea*; *Uncinula* species, for example *Uncinula necator*; *Microsphaera* species, for
15 example *Microsphaera diffusa*; *Leveillula* species, for example *Leveillula taurica*; *Erysiphe* species, for example *Erysiphe cichoracearum*;

diseases caused by rust disease pathogens, for example *Gymnosporangium* species, for example *Gymnosporangium sabinae*; *Hemileia* species, for example *Hemileia vastatrix*; *Phakopsora* species, for example *Phakopsora pachyrhizi* and *Phakopsora meibomia*; *Puccinia* species, for example *Puccinia recondite*, *P. triticea*, *P. graminis* or *P. striiformis*; *Uromyces* species, for example *Uromyces
20 appendiculatus*;

diseases caused by pathogens from the group of the *Oomycetes*, for example *Albugo* species, for example *Albugo candida*; *Bremia* species, for example *Bremia lactucae*; *Peronospora* species, for example *Peronospora pisi* or *P. brassicae*; *Phytophthora* species, for example *Phytophthora infestans*; *Plasmopara*
25 species, for example *Plasmopara viticola*; *Pseudoperonospora* species, for example *Pseudoperonospora humuli* or *Pseudoperonospora cubensis*; *Pythium* species, for example *Pythium ultimum*;

leaf blotch diseases and leaf wilt diseases caused, for example, by *Alternaria* species, for example *Alternaria solani*; *Cercospora* species, for example *Cercospora beticola*; *Cladosporium* species, for example *Cladosporium cucumerinum*; *Cochliobolus* species, for example *Cochliobolus sativus* (conidia form: Drechslera, Syn: Helminthosporium), *Cochliobolus miyabeanus*; *Colletotrichum* species, for example
30 *Colletotrichum lindemuthianum*; *Cycloconium* species, for example *Cycloconium oleaginum*; *Diaporthe* species, for example *Diaporthe citri*; *Elsinoe* species, for example *Elsinoe fawcettii*; *Gloeosporium* species,

for example *Gloeosporium laeticolor*; *Glomerella* species, for example *Glomerella cingulata*; *Guignardia* species, for example *Guignardia bidwelli*; *Leptosphaeria* species, for example *Leptosphaeria maculans*, *Leptosphaeria nodorum*; *Magnaporthe* species, for example *Magnaporthe grisea*; *Marssonina* species, for example *Marssonina coronaria*; *Microdochium* species, for example *Microdochium nivale*; *Mycosphaerella* species, for example *Mycosphaerella graminicola*, *M. arachidicola* and *M. fijiensis*; *Phaeosphaeria* species, for example *Phaeosphaeria nodorum*; *Pyrenophora* species, for example *Pyrenophora teres*, *Pyrenophora tritici repentis*; *Ramularia* species, for example *Ramularia collo-cygni*, *Ramularia areola*; *Rhynchosporium* species, for example *Rhynchosporium secalis*; *Septoria* species, for example *Septoria apii*, *Septoria lycopersii*; *Typhula* species, for example *Typhula incarnata*; *Venturia* species, for example *Venturia inaequalis*;

root and stem diseases caused, for example, by *Corticium* species, for example *Corticium graminearum*; *Fusarium* species, for example *Fusarium oxysporum*; *Gaeumannomyces* species, for example *Gaeumannomyces graminis*; *Rhizoctonia* species, such as, for example *Rhizoctonia solani*; *Sarocladium* diseases caused for example by *Sarocladium oryzae*; *Sclerotium* diseases caused for example by *Sclerotium oryzae*; *Tapesia* species, for example *Tapesia acuformis*; *Thielaviopsis* species, for example *Thielaviopsis basicola*;

ear and panicle diseases (including corn cobs) caused, for example, by *Alternaria* species, for example *Alternaria* spp.; *Aspergillus* species, for example *Aspergillus flavus*; *Cladosporium* species, for example *Cladosporium cladosporioides*; *Claviceps* species, for example *Claviceps purpurea*; *Fusarium* species, for example *Fusarium culmorum*; *Gibberella* species, for example *Gibberella zeae*; *Monographella* species, for example *Monographella nivalis*; *Septoria* species, for example *Septoria nodorum*;

diseases caused by smut fungi, for example *Sphacelotheca* species, for example *Sphacelotheca reiliana*; *Tilletia* species, for example *Tilletia caries*, *T. controversa*; *Urocystis* species, for example *Urocystis occulta*; *Ustilago* species, for example *Ustilago nuda*, *U. nuda tritici*;

fruit rot caused, for example, by *Aspergillus* species, for example *Aspergillus flavus*; *Botrytis* species, for example *Botrytis cinerea*; *Penicillium* species, for example *Penicillium expansum* and *P. purpurogenum*; *Sclerotinia* species, for example *Sclerotinia sclerotiorum*; *Verticillium* species, for example *Verticillium albo-atrum*;

seed and soilborne decay, mould, wilt, rot and damping-off diseases caused, for example, by *Alternaria* species, caused for example by *Alternaria brassicicola*; *Aphanomyces* species, caused for example by *Aphanomyces euteiches*; *Ascochyta* species, caused for example by *Ascochyta lentis*; *Aspergillus* species, caused for example by *Aspergillus flavus*; *Cladosporium* species, caused for example by *Cladosporium herbarum*; *Cochliobolus* species, caused for example by *Cochliobolus sativus*; (Conidiaform: Drechslera,

Bipolaris Syn: Helminthosporium); *Colletotrichum* species, caused for example by *Colletotrichum coccodes*; *Fusarium* species, caused for example by *Fusarium culmorum*; *Gibberella* species, caused for example by *Gibberella zeae*; *Macrophomina* species, caused for example by *Macrophomina phaseolina*; *Monographella* species, caused for example by *Monographella nivalis*; *Penicillium* species, caused for example by
 5 *Penicillium expansum*; *Phoma* species, caused for example by *Phoma lingam*; *Phomopsis* species, caused for example by *Phomopsis sojae*; *Phytophthora* species, caused for example by *Phytophthora cactorum*; *Pyrenophora* species, caused for example by *Pyrenophora graminea*; *Pyricularia* species, caused for example by *Pyricularia oryzae*; *Pythium* species, caused for example by *Pythium ultimum*; *Rhizoctonia* species, caused for example by *Rhizoctonia solani*; *Rhizopus* species, caused for example by *Rhizopus*
 10 *oryzae*; *Sclerotium* species, caused for example by *Sclerotium rolfsii*; *Septoria* species, caused for example by *Septoria nodorum*; *Typhula* species, caused for example by *Typhula incarnata*; *Verticillium* species, caused for example by *Verticillium dahliae*;

cancers, galls and witches' broom caused, for example, by *Nectria* species, for example *Nectria galligena*;

wilt diseases caused, for example, by *Monilinia* species, for example *Monilinia laxa*;

15 leaf blister or leaf curl diseases caused, for example, by *Exobasidium* species, for example *Exobasidium vexans*;

Taphrina species, for example *Taphrina deformans*;

decline diseases of wooden plants caused, for example, by Esca disease, caused for example by *Phaemoniella clamydospora*, *Phaeoacremonium aleophilum* and *Fomitiporia mediterranea*; Eutypa dyeback, caused for
 20 example by *Eutypa lata* ; Ganoderma diseases caused for example by *Ganoderma boninense*; Rigidoporus diseases caused for example by *Rigidoporus lignosus*;

diseases of flowers and seeds caused, for example, by *Botrytis* species, for example *Botrytis cinerea*;

diseases of plant tubers caused, for example, by *Rhizoctonia* species, for example *Rhizoctonia solani*; *Helminthosporium* species, for example *Helminthosporium solani*;

25 Club root caused, for example, by *Plasmodiophora* species, for example *Plasmodiophora brassicae*;

diseases caused by bacterial pathogens, for example *Xanthomonas* species, for example *Xanthomonas campestris* pv. *oryzae*; *Pseudomonas* species, for example *Pseudomonas syringae* pv. *lachrymans*; *Erwinia* species, for example *Erwinia amylovora*.

Fungal diseases on leaves, stems, pods and seeds caused, for example, by *Alternaria* leaf spot (*Alternaria*
 30 *spec. atrans tenuissima*), Anthracnose (*Colletotrichum gloeosporoides dematium* var. *truncatum*), brown

spot (*Septoria glycines*), cercospora leaf spot and blight (*Cercospora kikuchii*), choanephora leaf blight (*Choanephora infundibulifera trispora* (Syn.)), dactuliophora leaf spot (*Dactuliophora glycines*), downy mildew (*Peronospora manshurica*), drechslera blight (*Drechslera glycini*), frog-eye leaf spot (*Cercospora sojina*), leptosphaerulina leaf spot (*Leptosphaerulina trifolii*), phyllosticta leaf spot (*Phyllosticta sojaecola*),
 5 pod and stem blight (*Phomopsis sojae*), powdery mildew (*Microsphaera diffusa*), pyrenochaeta leaf spot (*Pyrenochaeta glycines*), rhizoctonia aerial, foliage, and web blight (*Rhizoctonia solani*), rust (*Phakopsora pachyrhizi*, *Phakopsora meibomia*), scab (*Sphaceloma glycines*), stemphylium leaf blight (*Stemphylium botryosum*), target spot (*Corynespora cassiicola*).

Fungal diseases on roots and the stem base caused, for example, by black root rot (*Calonectria crotalariae*),
 10 charcoal rot (*Macrophomina phaseolina*), fusarium blight or wilt, root rot, and pod and collar rot (*Fusarium oxysporum*, *Fusarium orthoceras*, *Fusarium semitectum*, *Fusarium equiseti*), mycoleptodiscus root rot (*Mycoleptodiscus terrestris*), neocosmospora (*Neocosmospora vasinfecta*), pod and stem blight (*Diaporthe phaseolorum*), stem canker (*Diaporthe phaseolorum* var. *caulivora*), phytophthora rot (*Phytophthora megasperma*), brown stem rot (*Phialophora gregata*), pythium rot (*Pythium aphanidermatum*, *Pythium irregulare*, *Pythium debaryanum*, *Pythium myriotylum*, *Pythium ultimum*),
 15 rhizoctonia root rot, stem decay, and damping-off (*Rhizoctonia solani*), sclerotinia stem decay (*Sclerotinia sclerotiorum*), sclerotinia southern blight (*Sclerotinia rolfii*), thielaviopsis root rot (*Thielaviopsis basicola*).

Preferred diseases of plants or crops that can be controlled by the method according to the invention, are:

Oomycete diseases such as

20 *Peronospora* diseases caused for example by *Peronospora tabacina*;

Phytophthora diseases caused for example by *Phytophthora infestans*;

Plasmopara diseases caused for example by *Plasmopara viticola*.

Most preferred diseases of plants or crops that can be controlled by the method according to the invention, are:

25 *Plasmopara* diseases caused for example by *Plasmopara viticola*.

Furthermore combinations and compositions according to the invention may also be used to reduce the contents of mycotoxins in plants and the harvested plant material and therefore in foods and animal feed stuff made therefrom.

Especially but not exclusively the following mycotoxins can be specified:

Deoxynivalenole (DON), Nivalenole, 15-Ac-DON, 3-Ac-DON, T2- und HT2- Toxins, Fumonisin, Zearalenone Moniliformine, Fusarine, Diacetoxyscirpenole (DAS), Beauvericine, Enniatine, Fusaroproliferine, Fusarenole, Ochratoxines, Patuline, Ergotalkaloides und Aflatoxines, which are caused for example by the following fungal diseases: *Fusarium spec.*, like *Fusarium acuminatum*, *F. avenaceum*, *F. crookwellense*, *F. culmorum*, *F. graminearum* (*Gibberella zeae*), *F. equiseti*, *F. fujikoroii*, *F. musarum*, *F. oxysporum*, *F. proliferatum*, *F. poae*, *F. pseudograminearum*, *F. sambucinum*, *F. scirpi*, *F. semitectum*, *F. solani*, *F. sporotrichoides*, *F. langsethiae*, *F. subglutinans*, *F. tricinctum*, *F. verticillioides* and others but also by *Aspergillus spec.*, *Penicillium spec.*, *Claviceps purpurea*, *Stachybotrys spec.* and others.

The very good fungicidal effect of the combinations or compositions according to the invention is shown in the following example. While the single active compounds do show weaknesses in their fungicidal efficacy, the combinations or compositions show an effect which is greater than the single addition of the efficacies of each compound.

According to another aspect of the present invention, in the combination or composition according to the invention, the compound ratio A/B, A/C or A/B/C may be advantageously chosen so as to produce a synergistic effect. A synergistic effect of fungicides is always present when the fungicidal activity of the active compound combinations exceeds the total of the activities of the active compounds when applied individually. The expected activity for a given combination of two or three active compounds can be calculated as follows (cf. Colby, S.R., "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations", Weeds 1967, 15, 20-22).

The latter article mentions the formula for combinations of 2 active compounds:

$$E_1 = X + Y - \frac{X \cdot Y}{100}$$

and the formula for a combination of 3 active compounds:

$$E_2 = X + Y + Z - \frac{X \cdot Y + X \cdot Z + Y \cdot Z}{100} + \frac{X \cdot Y \cdot Z}{10000}$$

wherein

- 25 X denotes the efficacy when using active compound A at an application rate of m ppm (or g/ha),
- Y denotes the efficacy when using active compound B (or C) at an application rate of n ppm (or g/ha),
- Z denotes the efficacy when using active compound C at an application rate of r ppm (or g/ha),

E1 denotes the efficacy when using active compounds A and B at application rates of m and n ppm (or g/ha), and

E2 denotes the efficacy when using active compounds A and B and C at application rates of m and n and r ppm (or g/ha),

- 5 The term “synergistic effect” also means the effect defined by application of the Tammes method, “Isoboles, a graphic representation of synergism in pesticides”, Netherlands Journal of Plant Pathology, 70(1964), pages 73-80.

Here, the efficacy is determined in %. 0 % means an efficacy which corresponds to that of the control, whereas an efficacy of 100 % means that no infection is observed.

- 10 If the actual fungicidal action exceeds the calculated value, the action of the combination is superadditive, i.e. a synergistic effect is present. In this case, the actually observed efficacy must exceed the value calculated using the above formula for the expected efficacy (E1 or E2).

The invention is illustrated by the example below. The invention is not restricted to the example only.

Example: *in vivo* preventive test on *Phytophthora* test (tomatoes)

- 15 Solvent: 24.5 parts by weight of acetone
 24.5 parts by weight of dimethylacetamide
 Emulsifier: 1 part by weight of alkylaryl polyglycol ether

- To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the
 20 desired concentration.

To test for preventive activity, young plants are sprayed with the preparation of active compound at the stated rate of application. After the spray coating has dried on, the plants are inoculated with an aqueous spore suspension of *Phytophthora infestans*. The plants are then placed in an incubation cabinet at approximately 20°C and a relative atmospheric humidity of 100%.

- 25 The test is evaluated 3 days after the inoculation. 0% means an efficacy which corresponds to that of the untreated control, while an efficacy of 100% means that no disease is observed.

The table below clearly shows that the observed activity of the active compound combination according to the invention is greater than the calculated activity, i.e. a synergistic effect is present.

Table: *in vivo* preventive test on *Phytophthora* test (tomatoes)

Active compounds	Application rate of active compound in ppm a.i.	Efficacy in %	
		found*	calc.**
(A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate	0.04 0.02	70 55	
(B) fosetyl-aluminium	8 4	8 0	
(C) mancozeb	6.4 3.2	8 20	
(A) + (B) + (C) 1:200:160	0.04 + 8 + 6.4	80	74
(A) + (B) + (C) 1:200:160	0.02 + 4 + 3.2	73	64

* found = activity found

** calc. = activity calculated using Colby's formula

Example: *in vivo* preventive test on *Plasmopara* test (grapevines)

Solvent: 24.5 parts by weight of acetone

24.5 parts by weight of dimethylacetamide

5 Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration.

10 To test for preventive activity, young plants are sprayed with the preparation of active compound at the stated rate of application. After the spray coating has dried on, the plants are inoculated with an aqueous spore suspension of *Plasmopara viticola* and then remain for 1 day in an incubation cabinet at approximately 20°C and a relative atmospheric humidity of 100%. The plant is subsequently placed for 4 days in a greenhouse at approximately 21°C and a relative atmospheric humidity of approximately 90%. The plants are then misted and placed for 1 day in an incubation cabinet.

15 The test is evaluated 6 days after the inoculation. 0% means an efficacy which corresponds to that of the untreated control, while an efficacy of 100% means that no disease is observed.

The table below clearly shows that the observed activity of the active compound combination according to the invention is greater than the calculated activity, i.e. a synergistic effect is present.

Table: *in vivo* preventive test on *Plasmopara* test (grapevines)

Active compounds	Application rate of active compound in ppm a.i.	Efficacy in %	
		found*	calc.**
(A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate	0.02	0	
(B) fosetyl-aluminium	4	0	
(C) mancozeb	3.2	0	
(A) + (B) + (C) 1:200:160	0.02 + 4 + 3.2	56	0

* found = activity found

** calc. = activity calculated using Colby's formula

Claims:

1. Active compound combination comprising
 - (A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl} piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate and
 - 5 (B) Fosetyl-aluminium and
 - (C) at least one compound selected from the group consisting of Mancozeb or Metiram.
2. Active compound combination according to claim 1 comprising,
 - (A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl} piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate and
 - 10 (B) Fosetyl-aluminium and
 - (C) Mancozeb.
3. Active compound combination according to claim 1 comprising,
 - (A) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl} piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate and
 - 15 (B) Fosetyl-aluminium and
 - (C) Metiram.
4. A composition comprising a combination according to claims 1, 2 or 3.
5. A composition according to claim 4 further comprising adjuvants, solvents, carrier, surfactants or extenders.
- 20 6. Use of an active compound combination according to any of claims 1, 2 or 3 for the treatment of seed.
7. Seed that has been treated with an active compound combination according to any of claims 1, 2 or 3.
8. A method for curatively or preventively controlling the phytopathogenic fungi of plants or crops
25 comprising the use of an active compound combination according to any of claims 1, 2 or 3 or a composition according to claim 4 for control of powdery mildew diseases.

9. The method according to claim 8 characterized in that an active compound combination to any of claims 1, 2 or 3 or a composition according to claim 4 is applied to the seed, the plant, to fruits of plants or to the soil on which the plant grows or is supposed to grow.
10. Use of an active compound combination according to any of claims 1, 2 or 3 or a composition
5 according to claim 4 for treatment of diseases caused by powdery mildew pathogens.
11. Use according to claim 10 characterized in that an active compound combination according to any of claims 1, 2 or 3 or a composition according to claim 4 is applied to the seed, the plant, to fruits of plants or to the soil on which the plant grows or is supposed to grow.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/063669

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N43/78 A01N47/14 A01P3/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, BIOSIS, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/127704 A1 (BAYER IP GMBH [DE]) 6 September 2013 (2013-09-06) cited in the application (I-3)+15.24; page 65; table 3 (I-3)+5.25; page 72; table 9 (I-3)+5.25; page 77 page 1, paragraph 4 page 6, lines 21,22 page 7, line 32 page 14, lines 20,21,35	1-11
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

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