Abstract:

Title:

Synergistic compositions for the protection of agrarian crops and the use thereof

(57) Abstract: Synergistic compositions comprising: one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide (I), one or more components (B) having fungicidal insecticidal activity, and their use the control of harmful insects in agrarian crops.
The present invention relates to synergistic compositions for the protection of agricultural crops and use thereof.

In particular, object of the present invention are compositions comprising one compound belonging to the N-indanyl-pyrazolecarboxamides chemical class and one or more fungicidal or insecticidal compounds.

In the application of antiparasitic products for agricultural use, it is widely known to combine two or more products having a different mechanism of action and/or a different biological target, in order to broaden the action range of the mixtures with respect to the product used individually and to prevent the occurrence of resistance phenomena from the harmful organisms, phenomena which with time tend to reduce the effectiveness of the antiparasitic products used.


The applicant has now surprisingly found that
combining one specific fungicidal compound belonging to the class of N-indanyl-pyrazolecarboxamides with one or more compounds selected from a series of compounds having fungicidal or insecticidal activity, compositions are obtained having biological activities which are:

1) improved with respect to those expected on the basis of the activities of the products used alone;
2) superior to those achievable with the compositions disclosed in said prior art documents.

A first object of the present invention therefore relates to synergistic compositions for the protection of agricultural crops comprising:
- at least a component \([A]\) consisting of the compound of formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide

\[
\text{H} \text{F}_2\text{C} \quad \text{O} \quad \text{NH} \quad \text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{F} \\
\text{Me}
\]

(1)

wherein Me represents a methyl group C₃H₇-
- at least a component \([B]\) selected from fungicidal or insecticidal compounds belonging to one or more of the following groups of fungicidal and insecticidal compounds:
fungicidal compounds:
1) azoles;
2) amino-derivatives;
3) strobilurins;
4) specific anti-oidium compounds;

-2-
v) aniline-pyrimidines;
vi) benzimidazoles and analogues;
vii) dicarboximides;
viii) polyhalogenated fungicides;
ix) systemic acquired resistance (SAR) inductors;
x) phenylpyrroles;
xi) acylalanines;
xii) anti-peronosporic compounds;
xiii) dithiocarbamates;
xiv) arylamidines;
xv) phosphorous acid and its derivatives;
xvi) fungicidal copper compounds;
xvii) fungicidal amides;
xviii) nitrogen heterocycles;
insecticidal compounds:
xix) neonicotinoids;
xx) phenylpyrazoles;
xxi) pyrethroids;
xxii) carbamates;
xxiii) macrolides of microbial origin;
xxiv) insecticidal diamides;
xxv) trifluoromethylpyridyl derivatives.

The compound of formula (I) can be prepared:
1) by acid isomerization of N-(3-difluoromethyl-1-
25 methyl-1H-4-pyrazolecarbonyl)-6-fluoro-2,2,4-trimethyl-
1,2,3,4-tetrahydro-quinoline (II), according to
reaction scheme 1, and as described in Example 1:

\[ \text{scheme 1} \]
by condensation of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid or its derivative, of general formula (III), with 7-fluoro-1,1,3-trimethyl-4-aminoundane (IV), utilizing methods well known in organic chemistry, according to scheme 2:

**Scheme 2**

\[
\text{Scheme 2: } \quad \text{scheme 2}
\]

wherein \( X \) represents a group selected from OH, alkoxy \( \text{C}_1-\text{C}_6 \) or a halogen atom (preferably chlorine).

The intermediate of formula (II) is in turn obtained by condensation of a compound of general formula (III) with 6-fluoro-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline (V), according to scheme 3:

**Scheme 3**

\[
\text{Scheme 3: } \quad \text{scheme 3}
\]

wherein \( X \) represents a group selected from OH, alkoxy \( \text{C}_1-\text{C}_6 \) or a halogen atom (preferably chlorine).
The 3-difluoromethyl -1-methyl -lH-pyrazole- 4-carboxylic acid and its derivatives of general formula (III) are known products, described for example in the patent N. US 5,093,347.

The intermediate of formula (V) can be prepared, according to reaction scheme 4, by hydrogenation of 6-fluoro-2,2,4-trimethyl-1,2-dihydroquinoline (VI), in turn obtained according to a method described in Organic Synthesis, Coll. Vol. Ill, pag. 329, starting from acetone and 4-fluoroaniline:

Scheme 4

\[
\begin{align*}
&\text{F} &\text{F} \\
&\text{H}_2\text{N} &\text{H}_2\text{N} \\
&\text{2 COCH}_3 &\text{Me} \\
&\text{I}_2 &\text{Me} \\
&\text{Me} &\text{Me} \\
&\text{Me} &\text{H}_2\text{Pd/C} \\
&\text{H}_2 &\text{(V)}
\end{align*}
\]

In the aforesaid formulas (I)-(VI) Me represents a methyl group \( \text{CH}_3^- \).

The aminoundane of formula (IV) can be prepared, analogously to what described in the patent N. EP 0654464, by condensation of 6-fluoro-2,2,4-trimethyl-1,2-dihydroquinoline (VI) with a carboxylic acid or its derivative, hydrogenation on Pd/C, isomerization with sulfuric acid and hydrolysis of the amide bond with water in acetic acid.

The compound of formula (I) contains an asymmetric carbon atom in position 3 of the indanyl group and it is usually obtained as racemic mixture of the two enantiomers having configurations R and S (molar ratio R:S equal to 1:1). However, it is possible to prepare mixtures of the two enantiomers of the compound of
formula (I) wherein the ratio R:S is different from 1:1 (enriched mixtures).

Moreover, it is possible to prepare the single enantiomers R and S of the compound of formula (I) in substantially pure form (> 99,99% by weight).

The aforesaid enantiomeric enriched mixtures and the substantially pure single enantiomers can be prepared, for example, by condensing the compounds of general formula (III) with enriched or enantiomerically pure forms (substantially pure single enantiomers) of the aminoindane of formula (IV), according to the reaction scheme 2; enriched or enantiomerically pure forms of the aminoindane of formula (IV) can be in turn obtained through enantioselective reactions and/or chemical and/or chromatographic separation of the enantiomers, according to methods described in literature for analogous products, for example as disclosed in the aforesaid EP 0654464.

In the synergistic compositions of the present invention the compound of formula (I) can be a racemic mixture, (I)-RS, or an enriched mixture of one of the two enantiomers, or even a substantially pure specific enantiomer (I)-R or (I)-S.

In the case of enriched mixtures of the compound of formula (I), those enriched in the enantiomer R are preferred, preferably with an R:S ratio of the two
Among the two enantiomeric forms of the compound of formula (I), the substantially pure isomer R is preferred.

The compounds among which to select the component [B] of the synergistic compositions are here indicated with their common international ISO name; their chemical structures and CAS and IUPAC chemical names are reported on the Alan Wood's Website (www.alanwood.net), Compendium of Pesticide Common Names; for most compounds, these features are also reported, together with chemical-physical data and biological features, in the "Pesticide Manual", C.D.S. Tomlin, 15th Edition, 2009, British Crop Production Council Editor.


Components [B] preferred of the compositions object of the present invention are:

i) azoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, epoxyconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetra-conazole, triadimefon, triadimenol, triflumizole, triticonazole;

ii) amino-derivatives: aldimorph, dodine, dodemorph, fen-propimorph, fenpropidin, guazatine, iminoctadine, spiroxamine, tridemorph;

iii) strobiluris: azoxystrobin, dimoxystrobin, fluoxa-
strobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrameto-
strobin, pyraoxostrobin, trifloxystrobin;
iv) specific anti-oidium compounds: cyflufenamid,
flutianil, metrafenone, proquinazid, pyriofenone,
quinoxyfen;
v) aniline-pyrimidines: pyrimethanil, mepanipyrim,
cyprodinil;
vii) benzimidazoles and analogues: benomyl, carbendazim,
flubendazole, thiabendazole, thiophanate-methyl;
vii) dicarboximides: iprodione, procymidone;
viii) polyhalogenated fungicides: chlorothalonil, captan, captafol, folpet, dichlofuanid, tollylfluanid;
i) SAR inductors: acibenzolar, probenazole, isotianil,
tiadinil;
ix) phenylpyrroles: fenpiclonil, fludioxonil;
i) acylalanines: benalaxyl, benalaxyl-M, furalaxyl, metalaxyl, metalaxyl-M;
xii) anti-peronosporic compounds: ametoctradin,
amisulbrom, bentiavalicarb, cyazofamid, cymoxanil,
dimethomorph, ethaboxam, famoxadone, fenamidone,
flumetover, flumorph, fluopicolide, iprovalicarb,
mandipropamid, valifenalate;
xi) dithiocarbamates: maneb, mancozeb, propineb,
zineb;
xiv) arylamidines: N-ethyl-N-methyl-N' -[4- [3-(4-
chlorobenzyl)-1,2, 4-thiadiazolyl-5-oxy] -2, 5-xylyl ]-
formamidine;
xv) phosphorous acid and derivatives: fosetyl-
aluminium, potassium phosphite, sodium phosphite,
choline phosphite;
xvi) copper fungicides: copper (II) hydroxide, copper
oxychloride, copper (II) sulfate, Bordeaux mixture, copper salycilate \( \text{C}_7\text{H}_3\text{O}_3\text{-Cu} \), cuprous oxide \( \text{Cu}_2\text{O} \);
xvii) fungicidal amides: carproamid, fenhexamid, silthiofam, zoxamid, bixafen, boscalid, carboxin, fluopicolide, fluopyram, flutolanil, fluxapyroxad, furametpyr, isopyrazam, oxycarboxin, penflufen, penthiopyrad, sedaxane, thifluzamide;
xviii) nitrogen heterocycles: fenpyrazamine, fluazinam, pyribencarb, tebufloquin;
xix) neonicotinoids: acetamiprid, clothianidin, dinotefuran, flupyradiflurone, imidacloprid, nitenpyram, thiacloprid, thiametoxam;
xx) phenylpyrazoles: ethiprole, fipronil, flupiprole, pyrafloprole, pyriprole;
xxi) pyrethroids: bifenthrin, beta-cyfluthrin, lambda-cyhalothrin, cypermethrin, deltamethrin, tefluthrin;
xxii) carbamates: oxamyl, thiodicarb, carbosulfan, methiocarb, carbofuran;
xxiii) macrolides of microbial origin: abamectin, emamectin benzoate, spinetoram, spinosad;
xxiv) insecticidal diamides: chlorantraniliprole, cyantraniliprole, flubendiamide;
xxv) trifluoromethylpyridyl derivatives: flonicamid, sulfoxaflor.

Among the aforesaid, components [B] particularly preferred are:

i) cyproconazole, difenoconazole, epoxyconazole, flutriafol, penconazole, prochloraz, prothioconazole, tebuconazole, tetraconazole;

ii) fenpropimorph, spiroxamine;

iii) azoxystrobin, fluoxastrobine, kresoxim-methyl, picoxystrobin, pyraclostrobin, triflloxystrobin;
iv) metrafenone, proquinazid;
v) mepanipyrim, cyprodinil;
vi) iprodione, procymidone;
vii) carbendazim, thiophanate-methyl;
viii) chlorothalonil;
x) fludioxonil;
xi) benalaxyl, benalaxyl-M, metalaxyl-M;
xii) benthiavalicarb, cyazofamid, cymoxanil, dimetomorph, mandipropamid, valifenalate;
xvi) copper (II) hydroxide, copper oxychloride, copper (II) sulfate, copper salicylate C$_7$H$_6$O$_3$-Cu, cuprous oxide Cu$_2$O;
xix) clothianidin, imidacloprid, thiachloprid, thiametoxam;
xx) ethiprole, fipronil;
xxi) lambda-cyhalothrin, deltamethrin, tefluthrin;
xxiv) chlorantraniliprole, flubendiamide.

The weight ratios of components [A] and [B] in the compositions object of the present invention can vary within a wide range, even depending on the parasites to be controlled and on the single component [B] used (or the plurality of components [B] used), and are usually comprised between 1:20 and 20:1.

Preferred compositions are those comprising at least the following combinations of compounds:

C1: (I) -RS + tetraconazole;
C2: (I) -RS + tebuconazole;
C3: (I) -RS + cyproconazole;
C4: (I) -RS + difenoconazole;
C5: (I) -RS + epoxyconazole;
C6: (I) -RS + flutriafol;
C7: (I) -RS + penconazole;
C8: (I) -RS + prothioconazole;
C9: (I) -RS + prochloraz;
C10: (I) -RS + fenpropimorph;
C11: (I) -RS + spiroxamine;
C12: (I) -RS + azoxystrobin;
C13: (I) -RS + fluoxastrobin;
C14: (I) -RS + kresoxim-methyl;
C15: (I) -RS + picoxytrobin;
C16: (I) -RS + pyraclostrobin;
C17: (I) -RS + trifloxystrobin;
C18: (I) -RS + metrafenone;
C19: (I) -RS + proquinazid;
C20: (I) -RS + mepanipyrim;
C21: (I) -RS + cyprodinil;
C22: (I) -RS + iprodione;
C23: (I) -RS + procymidone;
C24: (I) -RS + carbendazim;
C25: (I) -RS + thiophanate-methyl;
C26: (I) -RS + chlorothalonil;
C27: (I) -RS + fludioxonil;
C28: (I) -RS + benalaxyl-M;
C29: (I) -RS + metalaxyl-M;
C30: (I) -RS + benthiavali carb;
C31: (I) -RS + cyazof amid;
C32: (I) -RS + cymoxanil;
C33: (I) -RS + dime thomorph;
C34: (I) -RS + mandipropamid;
C35: (I) -RS + valifenalate;
C36: (I) -RS + copper salicylate C7H₄O₃Cu;
C37: (I) -RS + cuprous oxide CU₂O;
C38: (I) -RS + clothianidin;
C39: (I) -RS + imidacloprid;
C40: (I) -RS + thiacloprid;
C41: (I) -RS + thiamethoxam;
C42: (I) -RS + ethiprole;
C43: (I) -RS + fipronil/
C44: (I) -RS + lambda-cyhalothrin;
C45: (I) -RS + deltamethrin;
C46: (I) -RS + tefluthrin;
C47: (I) -RS + chlorantraniliprole;
C48: (I) -RS + flubendiamide;
C49: (I) -RS + tetraconazole + azoxystrobin;
C50: (I) -RS + tebuconazole + azoxystrobin/
C51: (I) -RS + epoxyconazole + azoxystrobin;
C52: (I) -RS + cyproconazole + azoxystrobin;
C53: (I) -RS + propiconazole + azoxystrobin;
C54: (I) -RS + prothioconazole + azoxystrobin;
C55: (I) -RS + tetraconazole + picoxystrobin;
C56: (I) -RS + tebuconazole + picoxystrobin;
C57: (I) -RS + epoxyconazole + picoxystrobin;
C58: (I) -RS + cyproconazole + picoxystrobin;
C59: (I) -RS + propiconazole + picoxystrobin;
C60: (I) -RS + prothioconazole + picoxystrobin;
C61: (I) -RS + tetraconazole + kresoxim methyl;
C62: (I) -RS + tebuconazole + kresoxim methyl;
C63: (I) -RS + epoxyconazole + kresoxim methyl;
C64: (I) -RS + cyproconazole + kresoxim methyl;
C65: (I) -RS + propiconazole + kresoxim methyl;
C66: (I) -RS + prothioconazole + kresoxim methyl;
C67: (I) -RS + chlorothalonil + azoxystrobin;
C68: (I) -RS + chlorothalonil + picoxystrobin;
C69: (I) -RS + chlorothalonil + pyraclostrobin;
C70: (I) -RS + chlorothalonil + kresoxim methyl;
C71: (I) -RS + copper (II) hydroxide + copper oxy-
chloride;
C72: (I)-RS + copper (II) hydroxide + copper oxy-
chloride + copper salicylate C\textsubscript{7}H\textsubscript{5}O3-Cu;
C73: (I)-RgS2 + tetraconazole;
C74: (I)-RgS2 + azoxystrobin;
C75: (I)-RgS\textsubscript{2} + benalaxyl;
C76: (I)-RgSi + tetraconazole;
C77: (I)-RgSi + azoxystrobin;
C78: (I)-R + tetraconazole;
wherein:
- (I)-RS represents the compound of formula (I) in form
of racemic mixture,
- (I)-RsS2 represents the compound having the
enantiomers R and S in molar ratio R:S = 8:2,
- (I)-RgSi represents the compound having the
enantiomers R and S in molar ratio R:S = 9:1,
- (I)-R represents the enantiomer R in substantially
pure form (>99, 99 weight %).

Preferably, in said compositions C1-C25, C27-C35,
C38-C48 e C73-C77 the weight ratio of components [A] e
[B] ranges from 1:20 to 20:1.

Preferably, in said compositions C26, C36, C37 the
weight ratio of components [A] e [B] ranges from 1:20
to a 20:10.

Preferably, in said compositions C49-C69 the
weight ratio of component [A] with respect to the two
components [B] ([A] : [B\textsubscript{1}] : [B\textsubscript{2}]) ranges from 1:20:20 to
20:1:1.

Preferably, in said composition C70 the weight
ratio of component [A] with respect to the two
components [B] ([A] : [B\textsubscript{1}] : [B\textsubscript{2}]) ranges from 1:20:20 to
20:10:1, whereas in C71 the ratio [A] : [B\textsubscript{1}] : [B\textsubscript{2}] ranges
from 1:20:20 to 20:10:10.

Preferably, in said composition C72, the weight ratio of component \([A]\) with respect to the three components \([B]\) \([A] : [B_1] : [B_2] : [B_3]\) ranges from 1:20:20:10 to 20:10:10:10.

As said, the compositions object of the present invention exhibit a strong synergistic effect, which can be evaluated by applying the Colby's formula ("Weeds", 1967, 15, pag. 20-22):

\[
E_T = E_A + E_B - (E_A \times E_B / 100)
\]

wherein \(E_T\) is the expected efficacy percentage for the composition containing the compounds \(A\) and \(B\) at the dosages \(d_A + d_B\), \(E_A\) is the efficacy percentage observed for the component \(A\) at the dosage \(d_A\), \(E_B\) is the efficacy percentage observed for the component \(B\) at the dosage \(d_B\).

When the efficacy observed for the composition \(A + B\) \((E_{A+B})\) is higher than the efficacy expected according to the Colby's formula \((E_{A+B} / E_T > 1)\), there is the presence of a synergistic effect.

In case of ternary combinations, the Colby's formula becomes:

\[
E_T = E_A + E_{B_1} + E_{B_2} - (E_A \times E_{B_1} + E_A \times E_{B_2} + E_{B_1} \times E_{B_2} / 100) + (E_A \times E_{B_1} \times E_{B_2} / 10000)
\]

wherein \(E_T\) is the expected efficacy percentage for the composition containing the compounds \(A\), \(B_1\) and \(B_2\) at the dosages \(d_A + d_{B_1} + d_{B_2}\), \(E_A\) is the efficacy percentage observed for the component \(A\) at the dosage \(d_A\), \(E_{B_1}\) is the efficacy percentage observed for the component \(B_1\) at the dosage \(d_{B_1}\), \(E_{B_2}\) is the efficacy percentage observed for the component \(B_2\) at the dosage \(d_{B_2}\). When the efficacy observed for the composition \(A + B_1 + B_2\) \((E_{A+B_1+B_2})\) is higher than the efficacy expected according to the
Colby's formula \( \frac{E_{A+B1-B2}}{E_t} > 1 \), there is the presence of a synergistic effect.

Due to the high synergistic effects, the amplitude of the action range, the considerable reduction in resistance phenomena from the target microorganisms, the compositions object of the present invention are endowed with a very high fungicidal activity, which is exerted with respect to numerous phytopathogenic fungi attacking important agricultural crops.

Said compositions exert a fungicidal activity which can be curative, preventive or eradicant, and generally have a very low or null phytotoxicity on the treated crops.

It is therefore a further object of the present invention the use of the synergistic fungicidal compositions described above for the control of phytopathogenic fungi in agricultural crops.

Pseudoperonospora cubensis, Bremia lactucae.

The main crops that can be protected with the compositions according to the present invention comprise cereals (wheat, barley, rye, oats, rice, maize, sorghum, etc.), fruit trees (apples, pears, plums, peaches, almonds, cherries, bananas, grapes, strawberries, raspberries, blackberries, etc.), citrus trees (oranges, lemons, mandarins, grapefruit, etc.), legumes (beans, peas, lentils, soybean, etc.), vegetables (spinach, lettuce, asparagus, cabbage, carrots, onions, tomatoes, potatoes, eggplants, peppers, etc.), cucurbitaceae (pumpkins, zucchini, cucumbers, melons, watermelons, etc.), oleaginous plants (sunflower, rape, peanut, castor, coconut, etc.), tobacco, coffee, tea, cocoa, sugar beet, sugar cane, cotton.

In particular, the compositions of the present invention have proved to be particularly effective in the control of Plasmopara viticola on vines, Phytophthora infestans and Botrytis Cinerea on tomatoes, Puccinia recondita, Erysiphe graminis, Helminthosporium teres, Septoria nodorum and Fusarium spp. on cereals, in the control of Phakopsora pachyrhizi on soybean, in the control of Uromyces Appendiculatus on beans, in the control of Venturia inaequalis on apple-trees, in the control of Sphaerotheca fuliginea on cucumbers.

In addition, the compositions of the present invention are also effective in the control of phytopathogenic bacteria and viruses, such as, for example, Xanthomonas spp., Pseudomonas spp., Erwinia amylovora, the tobacco mosaic virus.
The compositions comprising at least a compound of formula (I) and, as component [B], at least an insecticidal compound selected from one or more of the aforesaid groups of compounds xix-xxv, besides to have an excellent fungicidal activity, also have an excellent insecticidal activity against numerous species of insects harmful to agricultural crops.

It is therefore a further object of the present invention the use of said compositions, comprising at least a compound of formula (I) and at least an insecticidal compound selected from or more of the aforesaid groups of compounds xix-xxv, for the control of harmful insects in agricultural crops.

Examples of insects which can be controlled with the above said compositions, are those belonging to the order of Hemiptera, Lepidoptera, Tysanoptera, Diptera, Coleoptera, Orthoptera, Hymenoptera: Aphis gossypii, Myzus persicae, Macrosiphum euphorbiae, Brevicoryne brassicae, Toxoptera citricidus, Trialeurodes vaporariorum, Bemisia tabaci, Aonidiella aurantii, Comstockaspis perniciosa, Unaspis citri, Psylla piri, Laodelphax striatellus, Nilaparvata lugens, Nephrotettix cincticeps, Nephrotettix virescens, Chilo suppressalis, Ostrinia spp., Spodoptera spp., Mamestra brassicae, Agrotis spp., Thricoplasia spp., Heliothis spp., Helicoverpa spp., Pieris spp., Adoxophyes spp., Grapholita molesta, Cydia spp., Phyllonorycter blancardella, Lymantria spp., Plutella xylostella, Pectinophora gossypiella, Hyphantria cunea, Thrips spp., Frankliniella spp., Dacus spp., Ceratitis capitata, Liriomyza trifolii, Anthonomus grandis, Callosobruchus chinensis, Diabrotica spp., Agriotes...

Even if the components [A] and [B] can be mixed and applied as such on the crops to be protected, for the practical use in agriculture, it is usually preferable to use the fungicidal compositions, according to the present invention, in the form of suitable phytosanitary formulations.

The component [A] and the components [B] can be formulated separately and mixed in the preselected diluent (for example water) at the moment of the treatment of the agricultural crops to be protected, or combined together in single formulation ready to use before treatment.

Both in the case of components formulated separately, and in the case of components [A] and [B] combined together in formulations ready to use, the formulations can be in the form of dry powders, wettable powders, emulsifiable concentrates, emulsions, micro-emulsions, pastes, granules, water-dispersible granules, solutions, suspensions, etc.: the selection of the type of formulation depends both on the characteristics of components A and B, and on the specific use.

The compositions are prepared with known methods, for example by diluting the active ingredients with a solid or liquid diluent, possibly in the presence of surfactants, dispersers, suspending agents, stabilizers, adjuvants, etc..

The following can be used, for example, as solid diluent or carriers: silica, kaolin, bentonite, talc, diatomaceous earth, dolomite, calcium carbonate,
magnesia, gypsum, clays, synthetic silicates, attapulgite, sepiolites.

The following can be used, for example, as solvents or liquid diluents, in addition to water, aromatic organic solvents (xyloles or alkylbenzole mixtures, chlorobenzene, etc.), paraffins (oil cuts), alcohols (methanol, propanol, butanol, octanol, glycerol, etc.), esters (ethyl acetate, isobutyl acetate, alkyl carbonates, alkyl esters of adipic acid, alkyl esters of glutaric acid, alkyl esters of succinic acid, alkyl esters of lactic acid, etc.), vegetable oils (rapeseed oil, sunflower oil, soybean oil, castor oil, corn oil, peanut oil, and their alkyl esters), ketones (cyclohexanone, acetone, acetoephonene, isophorone, ethyl amyl ketone, etc.), amides (N, N-dimethylformamide, N-methylpyrrolidone, etc.), sulfoxides and sulfones (dimethylsulf oxide, dimethyl-sulfone, etc.) and mixtures thereof.

Surfactants that can be used are sodium salts, calcium salts, potassium salts, triethylamine or triethanolamine of alkynaphthalensulfonates, polynaphthalenesulfonates, alkysulfonates, alkylarylsulfonates, polycarboxylates, sulfosuccinates, alkylsulfosuccinates, lignin sulfonates, alkyl sulfates; and again polyethoxylated fatty alcohols, polyethoxylated alkyl phenols, polyethoxylated esters of sorbitol, polyethoxylated polypropoxy (block copolymers), can be used.

The compositions can also contain special additives for particular purposes, for example antifreeze agents such as propylene glycol, or adhesives such as Arabic gum, polyvinyl alcohol,
polyvinylpyrrolidone, etc.

If desired, other active ingredients compatible with [A] and [B] can be added to the compositions, such as, for example, further fungicidal or insecticidal compounds different from components [B] described above, phytoregulators, antibiotics, herbicides, fertilizers and/or mixtures thereof.

Examples of fungicides, other than components [B], that can be included in the synergistic compositions object of the present invention are listed hereunder with their international ISO name: ampropylfos, anilazine, benodanil, blasticidin-S, bupirimate, buthiobate, chinomethionat, chloroneb, chlozolinate, debacarb, dichlone, diclobutrazol, diclomezine, dicloran, diclocymet, diethofencarb, diflumetorim, dimethirimol, dinocap, dipyrithione, ditalimfos, dithianon, edifenphos, ethirimol, ethoxyquin, etridiazole, fenaminosulf, fenapanil, fenarimol, fenfuram, fenoxanil, fentin, ferbam, ferimzone, fluoroimide, fluotrimazole, flusulfamide, hymexazol, hydroxy-quinoline sulfate, iprobenfos, isoprothiolane, kasugamycin, mancopper, mebenil, mepronil, meptyldinocap, methfuroxam, metiram, metsulfovax, natamycin, nitrothal-isopropyl, nuarimol, ofurace, oxadixyl, pefurazoate, pencycuron, pentachlorocephol enol and its salts, phthalide, piperalin, polyoxins, propamocarb, prothio carb, pyracarbolid, pyrazophos, pyribencarb, pyrifenthox, pyroquilon, pyroxyfur, quinacetol, quinazamid, quintozene, streptomycin, thiadifluor, thicyofen, thiram, tioxymid, tolclofos-methyl, triarimol, triazbutil, triazoxide, tricyclazole, triforine, validamycin, vinclozolin,
ziram, sulfur.

The total concentration of components [A] and [B] in said compositions can vary within a wide range; it generally ranges from 1% to 99% by weight with respect to the total weight of the composition, preferably from 5% to 90% by weight with respect to the total weight of the composition.

In order to protect the agricultural crops, the compositions object of the present invention can be applied to any part of the plant, or on the seeds before sowing, or on the ground in which the plant grows.

A further object of the present invention therefore relates to a method for the control of phytopathogenic fungi in agricultural crops, which comprises applying an effective dose of at least one synergistic fungicidal composition of the type described above on one or more parts of the plant to be protected (for example, on seedlings, leaves, fruits, stems, branches, roots) and/or on the seeds of said plants before sowing, and/or on the ground in which the plant grows.

A further aspect of the present invention is a method for the control of harmful insects in agricultural crops which comprises applying an effective dose of at least one synergistic fungicidal composition comprising at least a compound of formula (I) and at least an insecticidal compound selected from one or more of the groups of compounds xix-xxv described above, on one or more parts of the plant to be protected (for example, on seedlings, leaves, fruits, stems, branches, roots) and/or on the seeds of the plant.
said plants before sowing, and/or on the ground in which the plant grows.

Preferred way of application for the compositions comprising the compound (I) and at least an 5 insecticidal compound selected from one or more groups of compounds xix-xxv is the seed-dressing.

The total amount of components [A] and [B] to be applied in order to obtain the desired effect can vary according to different factors such as, for example, the compounds used, the crop to be preserved, the type of pathogen or insect, the degree of infection, the climatic conditions, the application method, the formulation used.

Overall doses of components [A] and [B] ranging from 10 g to 5 kg per hectare of agricultural crop generally provide a sufficient control.

The following examples are provided for a better understanding of the invention, which should be considered as being illustrative and non-limiting of the same.

EXAMPLE 1
Preparation of the 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide (I)

A solution of 40 g of 3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carbonyl chloride [compound of formula (III); MW 194.5] in 40 ml of dichloroethane, is dropped at room temperature in a solution of 34 g of 6-fluoro-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline [compound of formula (V); MW 193] and 30 ml of triethylamine in 200 ml of dichloroethane.

After stirring for 3 hours at reflux, the reaction
mixture is poured in water (1,2 l) and extracted with dichloroethane. The organic layer is washed with 10% aqueous hydrochloric acid, anhydried with sodium sulfate, concentrated under vacuum to afford 58 g of a crude solid product corresponding to N-(3-difluoromethyl -1-methyl -1H-4-pyrazolecarbonyl )-6-fluoro-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline [compound of formula (II); GC-mass: M+ = 351].

To this crude product, 165 ml of 85% aqueous sulfuric acid are added and the mixture is then heated under stirring at 60°C for 30 minutes. After cooling the mixture is poured into water and ice, and extracted with dichloromethane. The organic layer is then washed with water, with a saturated solution of sodium bicarbonate in water, and with a saturated solution of sodium chloride in water. The organic layer is anhydried with sodium sulfate and concentrated under vacuum: the residue is purified by chromatography on silica gel (eluent heptane/EtOAc 6:4) to give 48 g of a white solid with melting point 147°C, corresponding to the desired product in racemic form, (I)-RS. GC-mass: M+ = 351.

1H NMR (200 MHz, CDCl3) δ at: 1,43 (3H,d), 1,38 (3H,s), 1,44 (3H,s), 1,66 (1H,dd), 2,21 (1H,dd), 3,38 (1H m), 3,98 (3H,s), 6,81 (1H, bs), 6,95 (1H,t), 6,70. ( 1H, m), 7,81 (1H,bs), 8,03 (1H,bs)

EXAMPLE 2
Preparation of separated enantiomers of compound (I).

36.8 g (1 eq) of racemic 7-fluoro-1,1,3-trimethyl-4-aminoindane [compound (IV)] and 14.3 g (0.5 eq) of D-(25,35)-(−) -tartaric acid in methanol (30 ml) were
mixed and heated at 70 °C for 1 hour.

The mixture was left to cool to room temperature; a precipitate was formed and the mixture kept for one night at 4 °C. The formed solid was filtered off, washed with a small amount of methanol and re-crystallized from methanol for six times to afford 14.8 g of an off white solid, corresponding to the 7-fluoro-1, 1,3-trimethyl-4-aminoindane D-tartarate.

To the salt, a 5 % sodium hydroxide aqueous solution was added until pH > 10, and the mixture extracted three times with diethyl ether. The reunited organic layers were washed with water and brine. Then, dried over Na₂SO₄ and concentrated under reduced pressure to obtain 6.38 g of (-)-4-amino-7-fluoro-1,1,3-trimethylindane as a white powder (yield 17%); e.e. > 99% (HPLC).

To a solution of 600 mg of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid [compound (III)] and a catalytic amount of N,N-dimethylformamide in dichloromethane (7 mL), 450 mg of thionyl chloride were added dropwise. The mixture was refluxed for 2h. The reaction was monitored by GC/MS. The solvent was evaporated in vacuo. The crude acid chloride obtained was used in the following step.

A solution of the crude 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride in dichloroethane (6 mL) was added dropwise over a period of 10 minutes, under nitrogen atmosphere, to a solution of 660 mg of (-)-4-amino-7-fluoro-1,1,3-trimethylindane, a catalytic amount of 4-dimethylaminopyridine and 420 mg of triethylamine in dichloroethane (5 mL).

The mixture was stirred at room temperature
overnight. At completion of the reaction (monitored through GC-MS) the mixture was diluted with dichloromethane (20 mL) and cooled at 0°C; a solution (20 mL) of 5% HCl was added.

The layers were separated and the organic phase washed with 5% HCl solution (2 x 20 mL), water (2 x 20 mL) and brine, then dried over Na₂SO₄. The solvent was evaporated under reduced pressure to give 1.3 g of a pale yellow solid.

The crude product was purified by column chromatography (eluent: heptane/EtOAc 6:4) to give 1.1 g (yield 92%) of 99.5 % pure enantiomer (-) (e.e. > 99% determined by HPLC with chiral column) as a white solid with m.p. = 129-130°C.

GC-MS: M⁺ = 351; [α]D²⁰ = - 59.5° (CHCl₃, 1g/100 ml).

In analogous manner, starting from racemic 7-fluoro-1,1,3-trimethyl-4-aminoindane [compound (IV)] and L-(2R,3R)-(-)-tartaric acid, the 99.3 %pure enantiomer (+) was prepared (e.e. > 99% determined by HPLC with chiral column) : white solid with m.p. = 131-132°C.

GC-MS: M⁺ = 351; [α]D²⁰ = + 60.1° (CHCl₃, 1g/100 ml).

EXAMPLE 3

Determination of "in vitro" activities of racemic (I) and enantiomers against phytopathogenic microorganisms.

Under sterile conditions, the technical racemic (I), the (-) and (+) enantiomers (prepared in Example 2) under testing, were dissolved in dimethylsulf oxide and serially diluted 3-fold to obtain a growth...
inhibition curve. Aqueous treatment solutions were prepared by adding DMSO stocks to water and mixing by pipet resulting in 2x final treatment concentration and 2x final DMSO concentration of 1.6%.

Sporulating plates of phytopathogenic microorganisms were harvested under sterile conditions in ½ strength Potato Dextrose Broth. Spores were filtered with cheesecloth and diluted to about 40000 spores per ml. Spores were aliquotted into 96 well microtiter plates at 150 microliters of spore suspension per well. Pathogenic spore suspensions were then treated with the 2x aqueous treatment solution or 1.6% DMSO for controls to give 1x final concentration or 0.8% DMSO. Plates were then held for 43 hours at room temperature.

After 43 hours at room temperature, plates were visually assessed microscopically for spore germination and growth inhibition. Plates were also quantitatively measured for growth inhibition by measuring optical density on a spectrophotometric plate reader at 405 nanometer wavelength. Optical density was corrected for absorbance of the media and active ingredient by subtracting the 405 nm readings for the 2x aqueous treatment solution or DMSO solution diluted with 1/2 strength POTATO DEXTROSE BROTH and no spores.

The % growth inhibition of the pathogen obtained for the technical racemic (I), (-) and (+) enantiomers was calculated according to the formula:

Percent Inhibition = ((1 - (OD trt - OD trt blank) / (OD untreated - OD untreated blank)) x 100)
wherein OD trt is the optical density at 405 nm for the spore suspension plus aqueous treatment solution and OD trt blank is the optical density at 405 nm for the 2x aqueous treatment solution plus ½ strength POTATO DEXTROSE BROTH and no spores and OD untreated is the optical density at 405 nm for the spores plus 1.6% DMSO and OD untreated blank is the optical density at 405 nm for the 1.6% DMSO plus ½ strength POTATO DEXTROSE BROTH and no spores. Values are the average of three replicates. Concentrations of the racemic, (-) and (+) enantiomers giving 50% growth inhibition (pI50) were calculated using GraphPad Prism software. Percent inhibition values were calculated using GraphPad Prism software Version 4.

Microorganisms tested were Botrytis cinerea (BC), Stagonospora nodorum (SN) and Magnaporthe griseae (MG).

The results are reported in Table 1.

Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>BC pI50 (ppm)</th>
<th>SN pI50 (ppm)</th>
<th>MG pI50 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Racemic (I)</td>
<td>0.32</td>
<td>1.1</td>
<td>0.72</td>
</tr>
<tr>
<td>(-)-(I)</td>
<td>0.17</td>
<td>0.42</td>
<td>0.46</td>
</tr>
<tr>
<td>(+)-(I)</td>
<td>n.i.</td>
<td>72</td>
<td>4.6</td>
</tr>
</tbody>
</table>

n.i. = no inhibition

EXAMPLE 4

Determination of the fungicidal activity in preventive application (5 days) against Puccinia recondita on wheat.
Leaves of wheat plants of the Salgemma variety, grown in pots in a conditioned environment kept at 20°C and 70% of relative humidity (R.H.), were treated by spraying both sides of the leaves with the compounds and the compositions under testing, dispersed in hydroacetic solutions at 20% by volume of acetone.

After remaining 5 days in a conditioned environment, the plants were sprayed on both sides of the leaves with an aqueous suspension of conidia of Puccinia recondita (2 mg of inoculum per 1 ml of solution for infection).

After being sprayed, the plants were kept in a humidity-saturated environment at a temperature ranging from 18 to 24°C for the incubation period of the fungus (1 day).

After this period, the plants were put in a greenhouse with R.H. of 70% and at a temperature of 18-24 °C for 14 days.

At the end of this period the external symptoms of the pathogen appeared and it was therefore possible to proceed with the visual assessment of the intensity of the infection. The fungicidal activity was expressed as percentage of reduction of affected leaves areas with respect to those of untreated plants used as control: the scale comprised, as extremes, the value 100 (full activity; healthy plant) and the value 0 (no activity; completely infected plant).

At the same time, the phytotoxicity (percentage of leaf necrosis) induced on the wheat plants by the
application of the products and compositions was evaluated: in this case, the scale ranged from 0 (no phytotoxicity) to 100 (completely necrotized plant).

In Table 2, the activities of racemic (I) and pure enantiomers of compound (I), prepared in Example 2, are reported.

Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate (ppm)</th>
<th>% Activity</th>
<th>% Phytotoxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Racemic (I)</td>
<td>125</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>62.5</td>
<td>96</td>
<td>0</td>
</tr>
<tr>
<td>(-)-(I)</td>
<td>125</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>(+)-(I)</td>
<td>125</td>
<td>45</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>62.5</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

The synergism of the compositions (A+B) under testing was evaluated according to the Colby's formula:

\[
E_T = E_A + E_B - (E_A \times E_B / 100)
\]

wherein \(E_T\) is the expected efficacy percentage for the composition containing the compounds A and B at the dosages \(d_A + d_B\), \(E_A\) is the efficacy percentage observed for the component A at the dosage \(d_A\), \(E_B\) is the efficacy percentage observed for the component B at the dosage \(d_B\).

When the efficacy observed for the composition A+B (\(E_{A+B}\)) is higher than the efficacy expected according to the Colby's formula (\(E_{A+B} / E_T > 1\)), a synergistic effect is confirmed.
EXAMPLE 5

Determination of synergistic effects "in vitro" against phytopathogenic microorganisms.

Under sterile conditions, the products and the compositions under testing were dissolved in dimethylsulf oxide, diluted with water and added under vigorous stirring to POTATO DEXTROSE AGAR, kept in a thermostatic bath at 55°C. The AGAR preparations, containing the compounds and the compositions under testing at the desired rates, were poured into 60 mm diameter Petri dishes (three for each product and composition) and left to cool to ambient temperature.

After solidification of the agarized medium, AGAR disks having 6 mm of diameter and supporting the micelyum of the microorganism, were placed in the centre of the Petri dishes; Petri dishes containing untreated POTATO DEXTROSE AGAR were also inoculated with the microorganism and used as control.

After incubation at 28°C, when control colonies had grown over 30 mm in diameter, but without reaching the edge of the dishes, the diameters of the developed colonies in treated and untreated dishes were measured; the percentage growth inhibition of the microorganism obtained with products and compositions was calculated according to the formula:

\[ I = (1 - z_i/z_0) \times 100 \]

wherein \( z_i \) is the diameter (average of three replicates) of the colonies treated with compounds and mixtures and \( z_0 \) is the diameter (average of three replicates) of...
untreated colonies.

Microorganisms tested were Botrytis cinerea, Fusarium culmorum, Helminthosporium teres, Pyricularia oryzae, Septoria nodorum, Venturia inaequalis.

The synergism of a binary mixture \((A + B)\) at the dose \((d_A + d_B)\) was evaluated according to the Colby's formula:

\[
I_t = I_A + I_B - (IAXIB/100)
\]

wherein:

\(I_t\) is the % growth inhibition expected for the mixture;
\(I_A\) is the % growth inhibition observed for compound A at the dose \(d_A\);
\(I_B\) is the % growth inhibition observed for compound B at the dose \(d_B\).

When the % growth inhibition observed for the composition \((A+B)\) is higher than that calculated by the Colby's formula \((IA_B > I_t; IA_B/I_t > 1)\), a synergistic effect is confirmed.
CLAIMS

1. Synergistic compositions for the protection of agrarian crops comprising:
   - at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide

\[
\begin{align*}
\text{HF}_2\text{C} & \quad \text{O} \\
\text{N} & \quad \text{NH} \\
\text{Me} & \quad \text{Me} \\
\text{F} & \quad \text{Me}
\end{align*}
\]

wherein Me represents a C₄-methyl group,
   - at least one component [B] selected from compounds having a fungicidal or insecticidal activity belonging to one or more of the following groups of fungicidal and insecticidal compounds:
     - fungicidal compounds:
       i) azoles;
       ii) amino derivates;
       iii) strobylurins;
       iv) specific anti-oidium compounds;
       v) anilinopyrimidines;
       vi) benzimidazoles and their analogues;
       vii) dicarboxyimides;
     - insecticidal compounds:
       viii) polyhalogenated fungicides;
       ix) inducers of acquired systemic resistance (SAR);
       x) phenylpyrroles;
       xi) acylalanines;
xii) antiperonosporic compounds;
xiii) dithiocarbamates;
xiv) arylamidines;
xv) phosphorous acid and its derivatives;
xvi) copper-based cupric fungicides;
xvii) fungicidal amides;
xviii) nitrogenated heterocycles;
insecticidal compounds:
xix) neonicotinoids;
xx) phenylpyrazoles;
xxi) pyrethroids;
xxii) carbamates;
xxiii) macrolides of a microbial origin;
xxiv) insecticidal diamides;
xxv) trifluoromethylpyridyl derivates.

2. The compositions according to claim 1, wherein said one or more components [B] are selected from compounds belonging to one or more of the following groups:

i) azoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, epoxyconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetra-conazole, triadimefon, triadimenol, triflumizole, triticonazole;

ii) amino derivates: aldimorph, dodine, dodemorph, fenpropimorph, fenpropidin, guazatine, iminoctadine, spiroxamine, tridemorph;

iii) strobylurins: azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysa-
strobin, picoxystrobin, pyraclostrobin, pyrameto-
strobin, pyraoxostrobin, trifloxystrobin;
iv) specific anti-oidium compounds: cyflufenamid,
flutianil, metrafenone, proquinazid, pyriofenone,
quinoxyfen;
v) anilinopyrimidines: pyrimethanil, mepanipyrim,
cyprodinil;
vi) benzimidazoles and their analogues: benomyl,
carbendazim, fuberidazole, thiabendazole, thiophanate-
methyl;
vii) dicarboxyimides: iprodione, procymidone;
viii) polyhalogenated fungicides: chlorothalonil,
captan, captafol, folpet, dichlofluanid, tolylfluanid;
ix) SAR inducers: acibenzolar, probenazole, isotianil,
tiadinil;
x) phenylpyrroles: fenpiclonil, fludioxonil;
xi) acylalanines: benalaxyl, benalaxyl-M, furalaxyl,
metalaxyl, metalaxyl-M;
xii) antiperonosporic compounds: ametoctradin,
amisulbrom, bentiavalicarb, cyazofamid, cymoxanil,
dimethomorph, ethaboxam, famoxadone, fenamidone,
flumetover, flumorph, fluopicolide, iprovalicarb,
mandipropamid, valifenalate;
xiii) dithiocarbamtes: maneb, mancozeb, propineb,
zineb;
xiv) arylamidines: N-ethyl-N-methyl-N'-(4-[(3- (4-chloro-
benzyl)-1,2,4-thiadiazolyl-5-oxy] -2, 5-xylyl )-formami-
dine;
xv) phosphorous acid and its derivatives: fosetyl-
aluminium potassium phosphite, sodium phosphite,
choline phosphate;
xvi) copper-based cupric fungicides: copper (II)
hydroxide, copper oxychloride, copper (II) sulfate, Bordeaux mixture, copper salicylate C₇H₄O₃Cu, cuprous oxide Cu₂O;

xvii) fungicidal amides: carpropamid, fenhexamid, silthiofam, zoxamid, bixafen, boscalid, carboxim, flucopicolide, fluopyram, flutolanil, fluxapyroxad, furametpyr, isopyrazam, oxcarboxin, penflufen, pentafluorpyrad, sedaxane, thifluzamide;

xviii) nitrogenated heterocycles: fenpyrazamine, fluazinam, pyribencarb, tebufluphoquin;

xix) neonicotinoids: acetamiprid, clothianidin, dinotefuran, flupyradifurone, imidacloprid, nitenpyram, thiacloprid, thiametoxam;

xx) phenylpyrazoles: ethiprole, fipronil, flufiprole, pyraf luprole, pyriprole;

xxi) pyrethroids: bifenthrin, beta-cyf luthrin, lambda-cyhalothrin, cypermethrin, deltamethrin, tefluthrin;

xxii) carbamates: oxamyl, thiodicarb, carbosulfan, methiocarb, carbofuran;

xxiii) macrolides of a microbial origin: abamectin, emamectin benzoate, spinetoram, spinosad;

xxiv) insecticidal diamides: chlorantraniliprole, cyantraniliprole, flubendiamide;

xxv) trifluoromethylpyridyl derivates: flonicamid, sulfoxaflor.

3. The compositions according to one or more of the previous claims, wherein said one or more components [B] are selected from compounds belonging to one or more of the following groups:

i) cyproconazole, difenoconazole, epoxyconazole, flutriafol, penconazole, prochloraz, prothioconazole, tebuconazole, tetraconazole;
ii) fenpropimorph, spiroxamine;
iii) azoxystrobin, fluoxastrobin, kresoxim-methyl, picoxystrobin, pyraclostrobin, trifloxystrobin;
iv) metrafenone, proquinazid;
v) mepanipyrim, cyprodinil;
vi) iprodione, procymidone;
vii) carbendazim, thiophanate-methyl;
viii) chlorothalonil;
x) fludioxonil;
xi) benalaxyl, benalaxyl-M, metalaxyl-M;
 xii) bentiavalicarb, cyazofamid, cymoxanil, dimetomorph, mandipropamid, valifenalate;
xvi) copper (II) hydroxide, copper oxychloride, copper salicylate C₇H₆O₃•Cu, cuprous oxide Cu₂O;
 xix) clothianidin, imidacloprid, thiachloprid, thiametoxam;
xx) ethiprole, fipronil;
xxi) lambda-cyhalothrin, deltamethrin, tefluthrin;
xxiv) chlorantraniliprole, flubendiamide.

4. The compositions according to one or more of the previous claims, wherein said compound having formula (I) is a racemic mixture ((I)-RS).

5. The compositions according to one or more of the claims from 1 to 3, wherein said compound having formula (I) is selected from:
- a mixture enriched in one of the enantiomers, preferably a mixture enriched in the enantiomer R,
- one of the two enantiomers R ((I)-R) or S ((I)-S) in a substantially pure form (>99, 99% by weight), preferably the enantiomer R.

6. The compositions according to one or more of the previous claims, wherein the weight ratio between said
at least one component [A] and said at least one component [B] ranges from 1:20 to 20:1.
7. The compositions according to one or more of the previous claims, selected from:

5  C1: CO -RS + tetraconazole;
    C2: CO -RS + tebuconazole;
    C3: (I) -RS + cyproconazole;
    C4: (I) -RS + difenoconazole;
    C5: (I) -RS + epoxyconazole;

10  C6: CO -RS + flutriafol;
    C7: (I) -RS + penconazole;
    C8: (I) -RS + prothioconazole;
    C9: (O -RS + prochloraz;
    C10: CO -RS + fenpropimorph;

15  C11: (I) -RS + spiroxamine;
    C12: (I) -RS + azoxystrobin;
    C13: (I) -RS + fluoxastrobin;
    C14: (I) -RS + kresoxim-methyl;
    C15: (I) -RS + picoxystrobin;

20  C16: (I) -RS + pyraclostrobin;
    C17: (I) -RS + trifloxystrobin;
    C18: (I) -RS + metrafenone;
    C19: (I) -RS + proquinazid;
    C20: (I) -RS + mepanipyrim;

25  C21: (I) -RS + cyprodinil;
    C22: (I) -RS + iprodione;
    C23: (I) -RS + procymidine;
    C24: (I) -RS + carbendazim;
    C25: (I) -RS + thiophanate-methyl;

30  C26: CO -RS + chlorothalonil;
    C27: CO -RS + fludioxonil;
    C28: CO -RS + benalaxyl-M;
C29: (I) -RS + metalaxyl-M;
C30: (I) -RS + ben thi aval icarb;
C31: (I) -RS + cyazof amid;
C32: (I) -RS + cymoxanil;
C33: (I) -RS + dimeth homor ph;
C34: (I) -RS + mandipropamid;
C35: (I) -RS + valifenalate;
C36: (I) -RS + copper salicylate \( C_7H_4O_3\cdot Cu \);
C37: (I) -RS + cuprous oxide \( Cu_2O \);
C38: (I) -RS + clothianidin;
C39: (I) -RS + imidacloprid;
C40: (I) -RS + thiacloprid;
C41: (I) -RS + thiamethoxam;
C42: (I) -RS + ethiprole /
C43: (I) -RS + fipronil;
C44: (I) -RS + lambda-cyalothrin;
C45: (I) -RS + deltamethrin;
C46: (I) -RS + tefluthrin;
C47: (I) -RS + chlorantraniliprole;
C48: (I) -RS + flubendiamide;
C49: (I) -RS + tetraconazole + azoxystrobin;
C50: (I) -RS + tebuconazole + azoxystrobin;
C51: (I) -RS + epoxyconazole + azoxystrobin;
C52: (I) -RS + cyproconazole + azoxystrobin;
C53: (I) -RS + propiconazole + azoxystrobin;
C54: (I) -RS + prothioconazole + azoxystrobin;
C55: (I) -RS + tetraconazole + picoxystrobin;
C56: (I) -RS + tebuconazole + picoxystrobin;
C57: (I) -RS + epoxyconazole + picoxystrobin;
C58: (I) -RS + cyproconazole + picoxystrobin;
C59: (I) -RS + propiconazole + picoxystrobin;
C60: (I) -RS + prothioconazole + picoxystrobin;
C61: (I) -RS + tetraconazole + kresoxim methyl;
C62: (I) -RS + tebuconazole + kresoxim methyl;
C63: (I) -RS + epoxyconazole + kresoxim methyl;
C64: (I) -RS + cyproconazole + kresoxim methyl;
C65: (I) -RS + propiconazole + kresoxim methyl;
C66: (I) -RS + prothioconazole + kresoxim methyl;
C67: (I) -RS + chlorothalonil + azoxystrobin;
C68: (I) -RS + chlorothalonil + picoxystrobin;
C69: (I) -RS + chlorothalonil + pyraclostrobin;
C70: (I) -RS + chlorothalonil + kresoxim methyl;
C71: (I) -RS + copper (II) hydroxide + copper oxychloride;
C72: (I) -RS + copper (II) hydroxide + copper oxychloride + copper salicylate C\textsubscript{7}H\textsubscript{6}O\textsubscript{3}-Cu;
C73: (I) -Re S\textsubscript{2} + tetraconazole;
C74: (I) -Re S\textsubscript{2} + azoxystrobin;
C75: (I) -Re S\textsubscript{2} + benalaxyl;
C76: (I) -Rg S\textsubscript{1} + tetraconazole;
C77: (I) -Rg S\textsubscript{1} + azoxystrobin;
C78: (I) -R + tetraconazole;

wherein:
- (I) -RS indicates the compound having formula (I) in the form of a racemic mixture,
- (I) -Rg S\textsubscript{1} indicates the compound containing the enantiomers R and S in a molar ratio R:S = 8:2,
- (I) -Rg S\textsubscript{2} indicates the compound containing the enantiomers R and S in a molar ratio R:S = 9:1,
- (I) -R indicates the enantiomer R in substantially pure form (>99, 99% by weight).

8. The compositions according to one or more of the previous claims, wherein said at least one component [A] and said at least one component [B], together or
separately, are diluted with one or more solid or liquid diluents, possibly with the addition of one or more surfactants, dispersing agents, suspending agents, stabilizers, adjuvants, anti-freeze agents, adhesion agents.

9. The compositions according to claim 8, comprising at least a further active principle, compatible with said components [A] and [B], selected from fungicidal compounds or insecticidal compounds different from said compounds [B], phytoregulators, antibiotics, herbicides, fertilizers and mixtures thereof.

10. Use of the compositions according to one or more of the previous claims for the control of phytopathogenic fungi in agricultural crops.


12. Use of the compositions according to claim 10 or 11, wherein the agrarian crops are selected from: cereals, fruit trees, citrus fruits, legumes,
horticultural crops, cucurbits, oleaginous plants, tobacco, coffee, tea, cocoa, sugar beet, sugar cane, cotton.

13. Use of synergistic compositions comprising:
- at least one component (A), consisting of the compound having formula (I) 3-difluoromethyl-N-(7-fluoro-1,1,3-trimethyl-4-indanyl)-1-methyl-4-pyrazolecarboxamide

wherein Me represents a C₄- methyl group,
- at least one component (B) selected from compounds having a fungicidal or insecticidal activity belonging to one or more of the following groups of fungicidal and insecticidal compounds:
  xix) neonicotinoids;
  xx) phenylpyrazoles;
  xxi) pyretroids;
  xxii) carbamates;
  xxiii) macrolides of a microbial origin;
  xxiv) insecticidal diamides;
  xxv) trifluoromethylpyridyl derivates,
for the control of harmful insects in agrarian crops.

14. A method for controlling phytopathogenic fungi in agrarian crops, which comprises applying an effective dose of at least one synergistic composition according
to any of the claims from 1 to 9, on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

15. A method for controlling harmful insects in agrarian crops, which comprises applying an effective dose of at least one synergistic composition as defined in claim 13, on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/EP2013/062306

**A. CLASSIFICATION OF SUBJECT MATTER**

| INV. | A01N35/04 | A01N37/34 | A01N37/36 | A01N37/38 | A01N37/46 | A01N37/50 | A01N43/30 | A01N43/36 | A01N43/40 | A01N43/50 | A01N43/54 | A01N43/56 | A01N43/653 | A01N43/84 | A01N43/88 |
|------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
|      |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |

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, CHEM ABS Data, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Relevant to claim No.</th>
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<td>WO 2011/135833 A1 (SUMITOMO CHEMICAL CO [JP]; MATSUZAKI YUICHI [JP]) 3 November 2011 (2011-11-03) paragraphs [0001] - [0006], [0009], [0011], [0016], [0103] - [0127] tables 1,3,5,7,9,11,13,15,17,19,21</td>
<td>1-12,14, 15</td>
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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
- **L** document which may throw doubts on priority claim(s) on which is cited to establish the publication date of another citation or other special reason (as specified)
- **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
- **A** document member of the same patent family

Date of the actual completion of the international search
9 July 2013

Date of mailing of the international search report
19/07/2013

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Zanobini, Alessandra
**INTERNATIONAL SEARCH REPORT**

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. □Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. X As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

□ The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

□ The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of azoles; use of the compositions for the control of phytopathogenic fungi in agricultural crops; a method for controlling phytopathogenic fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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2. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of amino derivatives; use of the compositions for the control of phytopathogenic fungi in agricultural crops; a method for controlling phytopathogenic fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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3. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of strobilurins; use of the compositions for the control of phytopathogenic fungi in agricultural crops; a method for controlling phytopathogenic fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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4. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of
the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of specific aminopyrimidine compounds; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agricultural crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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5. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agricultural crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of benzimidazoles and their analogues; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agricultural crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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6. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agricultural crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of di(carboxyimide); use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agricultural crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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7. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agricultural crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of di(carboxyimide); use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agricultural crops which comprises applying an effective dose of at least one synergistic composition on
one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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8. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of polyhalogenated fungi cides; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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9. claims: 1, 2, 4-6, 8-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of inducers of acquired systemic resistance (SAR); use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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10. claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of phenyl pyrrol es; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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11. claims: 1-12, 14 (al 1 partially)
Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of acyl alani nes; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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12. Claims: 1-12, 14 (all 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of anti-peronosporic compounds; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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13. Claims: 1, 2, 4-6, 8-12, 14 (all 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of di thiocarbamates; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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14. Claims: 1, 2, 4-6, 8-12, 14 (all 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of aryl amides; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen...
fungi in agraria n crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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15. Claims: 1, 2, 4-6, 8-12, 14 (al 1 partially)

Synergistic compositions for the protection of agraria n crops comprising at list one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of phosphorous acid and its derivatives; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agraria n crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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16. Claims: 1-12, 14 (al 1 partially)

Synergistic compositions for the protection of agraria n crops comprising at list one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of copper-based cupric fungicides; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agraria n crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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17. Claims: 1, 2, 4-6, 8-12, 14 (al 1 partially)

Synergistic compositions for the protection of agraria n crops comprising at list one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of fungicidal amides; use of the compositions for the control of phytopathogen fungi in agricultural crops; a method for controlling phytopathogen fungi in agraria n crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.
18. **Claims**: 1, 2, 4-6, 8-12, 14 (al 1 partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having a fungicidal activity belonging to the group of nitrogenated heterocycles; use of the compositions for the control of phytopathogenic fungi in agricultural crops; a method for controlling phytopathogenic fungi in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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19. **Claims**: l-15 (partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having an insecticidal activity belonging to the group of neonoti noids; use of the compositions for the control of harmful insects in agricultural crops; a method for controlling harmful insects in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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20. **Claims**: l-15 (partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having an insecticidal activity belonging to the group of phenylpyrazoles; use of the compositions for the control of harmful insects in agricultural crops; a method for controlling harmful insects in agrarian crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.

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21. **Claims**: l-15 (partially)

Synergistic compositions for the protection of agrarian crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having an insecticidal activity belonging to the group of pyrethroids; use of the
compositions for the control of harmful insects in agricul
tural crops; a method for control ling harmful insects in agrari an crops which comprises apply ng an effecti ve dose of at least one synergi sti c composition on one or more parts of the plants to be protected and/or on the seeds of sai d plants before sowing and/or on the ground in which sai d plants grow.

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22. clai ms: 1, 2, 4-6, 8-15 (al 1 parti al ly)

Synergi sti c compositions for the protecti on of agrari an crops comprising at list one component (A), consi sting of the compound having formul a (I), and at least one component [B] selected from compounds having an insecti cidal acti vity bel ongi ng to the group of carbamates; use of the compositions for the control of harmful insects in agricul
tural crops; a method for control ling harmful insects in agrari an crops which comprises apply ng an effecti ve dose of at least one synergi sti c composition on one or more parts of the plants to be protected and/or on the seeds of sai d plants before sowing and/or on the ground in which sai d plants grow.

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23. clai ms: 1, 2, 4-6, 8-15 (al 1 parti al ly)

Synergi sti c compositions for the protecti on of agrari an crops comprising at list one component (A), consi sting of the compound having formul a (I), and at least one component [B] selected from compounds having an insecti cidal acti vity bel ongi ng to the group of macrolides of a microbi al ori gin; use of the compositions for the control of harmful insects in agricul
tural crops; a method for control ling harmful insects in agrari an crops which comprises apply ng an effecti ve dose of at least one synergi sti c composition on one or more parts of the plants to be protected and/or on the seeds of sai d plants before sowing and/or on the ground in which sai d plants grow.

---

24. clai ms: 1-15 (parti al ly)

Synergi sti c compositions for the protecti on of agrari an crops comprising at list one component (A), consi sting of the compound having formul a (I), and at least one component [B] selected from compounds having an insecti cidal acti vity bel ongi ng to the group of insecti cidal dlanides; use of the compositions for the control of harmful insects in agricul
tural crops; a method for control ling harmful insects in agrari an crops which comprises apply ng an effecti ve dose of at least one synergi sti c composition on one or more parts of the plants to be protected and/or on the seeds of sai d plants before sowing and/or on the ground in which sai d plants grow.
25. claims: 1, 2, 4-6, 8-15 (all partially)

Synergistic compositions for the protection of agricultural crops comprising at least one component (A), consisting of the compound having formula (I), and at least one component [B] selected from compounds having insecticidal activity belonging to the group of trifluoromethyl pyridyl derivatives; use of the compositions for the control of harmful insects in agricultural crops; a method for controlling harmful insects in agricultural crops which comprises applying an effective dose of at least one synergistic composition on one or more parts of the plants to be protected and/or on the seeds of said plants before sowing and/or on the ground in which said plants grow.
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