FUNGICIDAL MIXTURES BASED ON PROTHIOCONAZOLE AND A STROBLURIN DERIVATIVE

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ABSTRACT

Disclosed is a fungicidal mixture containing (1) 2-[2-(1-chlorocyclo-propyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thion of formula (I) or the salts or adducts thereof, and at least one additional fungicidal compound or the salts or adducts thereof, selected among (2) trifloxystrobin of formula (II), (Prothioconazole) (3) picoxystrobin of formula (I), (4) pyraclostrobin of formula (IV), (5) dimoxystrobin of formula (V), and (6) a strobilurin derivative of formula (VI), in a synergistically active quantity.

![Chemical Structure](image-url)
FUNGICIDAL MIXTURES BASED ON PROTHIOCONAZOLE AND A STROBLURIN DERIVATIVE

[0001] The present invention relates to a fungicidal mixture, comprising

[0002] (1) 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione (prothioconazole) of the formula I or its salts or adducts

[0003] and at least one further fungicidal compound or its salts or adducts, selected from the group consisting of

[0004] (2) trifloxystrobin of the formula II

[0005] and

[0006] (3) picoxystrobin of the formula III

[0007] and

[0008] (4) pyraclostrobin of the formula IV

[0009] and

[0010] (5) dimoxystrobin of the formula V

[0011] and

[0012] (6) a strobilurin derivative of the formula VI

[0013] in a synergistically effective amount.

[0014] Moreover, the invention relates to a method for controlling harmful fungi using mixtures of the compounds I with at least one of the compounds II, III, IV, V or VI, and to the use of the compounds I, II, III, IV, V and VI for preparing such mixtures, and to compositions comprising such mixtures.

[0015] The compound of the formula I, 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione (prothioconazole), has already been disclosed in WO 96/16048.

[0016] A number of active compound combinations of prothioconazole with a large number of other fungicidal compounds have been disclosed in WO 98/47367.


[0019] The strobilurin derivative of the formula IV is likewise already known and has been described in EP-A-0 804 421.


[0021] Finally, the strobilurin derivative of the formula VI is likewise known and has been described in EP-A-0 876 332.

[0022] It is an object of the present invention to provide mixtures which have further improved activity against harmful fungi combined with a reduced total amount of active compounds applied (synergistic mixtures), with a view to reducing the application rates and improving the activity spectrum of the known compounds I, II, III, IV, V and VI.

[0023] We have found that this object is achieved by the mixture, defined at the outset, of prothioconazole with at least one strobilurin derivative. Moreover, we have found that applying the compound I and at least one of the compounds II, III, IV, V or VI simultaneously, i.e. together or separately, or applying the compound I and at least one of
the compounds II, III, IV, V or VI in succession provides better control of harmful fungi than is possible with the individual compounds alone.

[0024] 2-[2-(1-Chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro{1,2,4}-triazole-3-thione of the formula I is known from WO 96-16 048. The compound can be present in the “thiono” form of the formula

\[
\text{I} \quad \begin{array}{c}
\text{Cl} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{N} \\
\end{array}
\]

or in the tautomeric “mercapto” form of the formula

\[
\text{Ia} \quad \begin{array}{c}
\text{Cl} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{S} \\
\end{array}
\]

[0025] For the sake of simplicity, only the “thiono” form is shown in each case.

[0026] Trifloxystrobin of the formula II

\[
\text{II} \quad \begin{array}{c}
\text{Cl} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{N} \\
\text{O} \\
\text{C} \\
\end{array}
\]

(Trifloxystrobin)

[0027] is known from EP-A 0 460 572.

[0028] Picoxystrobin of the formula III

\[
\text{III} \quad \begin{array}{c}
\text{Cl} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{N} \\
\text{O} \\
\text{C} \\
\text{H}_3 \\
\end{array}
\]

(Picoxystrobin)


[0031] Pyraclostrobin of the formula IV

\[
\text{IV} \quad \begin{array}{c}
\text{Cl} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{N} \\
\text{O} \\
\text{C} \\
\end{array}
\]

(Pyraclostrobin)

[0032] is known from EP-A 0 804 421.

[0033] Dimoxystrobin of the formula V

\[
\text{V} \quad \begin{array}{c}
\text{Cl} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{N} \\
\text{O} \\
\text{C} \\
\text{H}_3 \\
\end{array}
\]

(Dimoxystrobin)

[0034] is known from EP-A 0 477 631.

[0035] The strobilurin derivative of the formula VI

\[
\text{VI} \quad \begin{array}{c}
\text{Cl} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_2 \\
\text{N} \\
\text{O} \\
\text{C} \\
\text{H}_3 \\
\end{array}
\]

(VI)

[0036] is known from EP-A 0 876 332.

[0037] Owing to the basic character of their nitrogen atoms, the compounds I to VI are capable of forming salts or adducts with inorganic or organic acids or with metal ions.

[0038] Examples of inorganic acids are hydrohalic acids, carbonic acid, such as hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide, sulfuric acid, phosphoric acid and nitric acid.

[0039] Suitable organic acids are, for example, formic acid, carbonic acid and alkanolic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glyoxylic acid, thioacetic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic acid, alkylsulfonic acids (sulfonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbon atoms), arylsulfonic acids or aryldisulfonic acids (aromatic radicals, such as phenyl and naphthyl, which carry one or two sulfonic acid groups), alkylyphosphonic acids (phosphonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbon atoms), arylphosphonic acids or arylalkylphosphonic acids (aromatic radicals, such as phenyl and naphthyl, which carry
one or two phosphonic acid radicals), it being possible for the alkyl or aryl radicals to carry further substituents, for example p-toluenesulfonic acid, salicylic acid, p-amino salicylic acid, 2-phenoxybenzoic acid, 2-acetoxybenzoic acid, etc.

[0040] Suitable metal ions are in particular the ions of the elements of the second main group, in particular calcium and magnesium, of the third and fourth main group, in particular aluminum, tin and lead, and of the first to eighth transition group, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc and others. Particular preference is given to the metal ions of the elements of the transition groups of the fourth period. The metals can be present in the various valencies that they can assume.

[0041] Preference is given to mixtures of prothioconazole with trifloxystrobin of the formula II.

[0042] Preference is also given to mixtures of prothioconazole with picoxystrobin of the formula III.

[0043] Preference is given to mixtures of prothioconazole with pyraclostrobin of the formula IV.

[0044] Preference is furthermore also given to mixtures of prothioconazole with dimoxystrobin of the formula V.

[0045] Preference is also given to mixtures of prothioconazole with the strobilurin derivative of the formula VI.

[0046] Preference is also given to three-component mixtures of prothioconazole with two of the abovementioned strobilurin derivatives.

[0047] When preparing the mixtures, it is preferred to employ the pure active compounds I, II, III, IV, V and VI, to which may be added further active compounds against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers.

[0048] The mixtures of the compound I with at least one of the compounds II, III, IV, V or VI or the compound I, used simultaneously, jointly or separately, with at least one of the compounds II, III, IV, V or VI exhibit outstanding activity against a wide range of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes. Some of them act systematically and can therefore also be employed as folio- and soil-acting fungicides.

[0049] They are especially important for controlling a large number of fungi in a variety of crop plants, such as cotton, vegetable species (e.g. cucumbers, beans, tomatoes, potatoes and cucurbit), barley, grass, oats, bananas, coffee, corn, fruit species, rice, rye, soya, grapevine, wheat, ornamentals, sugar cane, and a variety of seeds.

[0050] They are particularly suitable for controlling the following phytopathogenic fungi: Blumeria graminis (powder mildew) in cereals, Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits, Podosphaera leucotricha in apples, Uncinula necator in grapevines, Puccinia species in cereals, Rhizoctonia species in cotton, rice and lawns, Ustilago species in cereals and sugar cane, Venturia inaequalis (scab) in apples, Helminthosporium species in cereals, Septoria nodorum in wheat, Botrytis cinera (gray mold) in strawberries, vegetables, ornamentals and grapevines, Cercospora arachidicola in groundnuts, Pseudocercosporella herpotrichoides in wheat and barley, Pyricularia oryzae in rice, Phytophthora infestans in potatoes and tomatoes, Plasmopara viticola in grapevines, Pseudoperonospora species in hops and cucumbers, Alternaria species in vegetables and fruit, Mycosphaerella species in bananas and Fusarium and Verticillium species.

[0051] They can furthermore be employed in the protection of materials (e.g. the protection of wood), for example against Pseudolomyces variotii.

[0052] The compound I can be applied simultaneously, that is either together or separately, or successively with at least one of the compounds II, III, IV, V and VI, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

[0053] The compounds I and II are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

[0054] The compounds I and III are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

[0055] The compounds I and IV are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

[0056] The compounds I and V are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

[0057] The compounds I and VI are usually applied in a weight ratio of from 20:1 to 1:20, in particular from 10:1 to 1:10, preferably from 5:1 to 1:5.

[0058] Depending on the kind of effect desired, the application rates of the mixtures according to the invention are, in particular in agricultural crop areas, from 0.01 to 8 kg/ha, preferably from 0.1 to 5 kg/ha, in particular from 0.1 to 3 kg/ha.

[0059] The application rates for the compound I are from 0.01 to 1 kg/ha, preferably from 0.05 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

[0060] Correspondingly, in the case of the compound II, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

[0061] Correspondingly, in the case of the compound III, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

[0062] Correspondingly, in the case of the compound IV, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

[0063] Correspondingly, in the case of the compound V, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

[0064] Correspondingly, in the case of the compound VI, the application rates are from 0.01 to 1 kg/ha, preferably from 0.02 to 0.5 kg/ha, in particular from 0.05 to 0.3 kg/ha.

[0065] For seed treatment, the application rates of the mixture are generally from 0.001 to 250 g/kg of seed, preferably from 0.01 to 100 g/kg of seed, in particular from 0.01 to 50 g/kg.
If phytopathogenic harmful fungi are to be controlled, the separate or joint application of the compound I with at least one of the compounds II, III, IV, V and VI or of the mixtures of the compound I with at least one of the compounds II, III, IV, V or VI is effected by spraying or dusting the seeds, the plants or the soils before or after sowing of the plants, or before or after plant emergence.

The fungicidal synergistic mixtures according to the invention or the compound I and at least one of the compounds II, III, IV, V and VI can be formulated, for example, in the form of ready-to-spray solutions, powders and suspensions or in the form of highly concentrated aqueous, oily or other suspensions, dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting or granules, and applied by spraying, atomizing, dusting, broadcasting or watering. The use form depends on the intended purpose; in each case, it should ensure as fine and uniform as possible a distribution of the mixture according to the invention.

The formulations are prepared in a known manner, for example by adding solvents and/or carriers. Usually, inert additives, such as emulsifiers or dispersants, are added to the formulations.

Suitable surfactants are the alkaline metal salts, alkali earth metals salts and ammonium salts of aromatic sulfonic acids, for example ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, alkyl- and allylarylsulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa- and octadecanols, or of fatty alcohol glycerol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isoctyl-, octyl- or nonylphenol, alkylphenol or tributylphenyl polyglycol ethers, alkylary polyether alcohols, isostearyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or jointly grinding the compound I and at least one of the compounds II, III, IV, V and VI or the mixture of the compound I with at least one compound II, III, IV, V or VI with a solid carrier.

Granules (for example coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active compound, or active compounds, to a solid carrier.

Fillers or solid carriers are, for example, mineral earths such as silica gel, silicas, silicates, tala, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, and also fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, urea, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

The formulations generally comprise from 0.1 to 95% by weight, preferably from 0.5 to 90% by weight, of the compound I and at least one of the compounds II, III, IV, V or VI or of the mixture of the compound I with at least one compound II, III, IV, V or VI. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum or HPLC).

The compound I and at least one of the compounds II, III, IV, V and VI or the mixtures or the corresponding formulations are applied by treating the harmful fungi, their habitat, or the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture, or of the compound I and at least one of the compounds II, III, IV, V or VI in the case of separate application.

Application can be effected before or after infection by the harmful fungi.

USE EXAMPLE

The synergistic activity of the mixtures according to the invention could be demonstrated by the following experiments:

The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 63% by weight of cyclohexanone and 27% by weight of emulsifier, and diluted with water to the desired concentration.

Evaluation was carried out by determining the infected leaf areas in percent. These percentages were converted into efficacies. The efficacy (W) was determined as follows using Abbot’s formula:

\[ W = \left(1 - \frac{a}{b}\right) \times 100 \]

\[ \alpha \] corresponds to the fungal infection of the treated plants in % and

\[ \beta \] corresponds to the fungal infection of the untreated (control) plants in %

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

The expected efficacies of the mixtures of the active compounds were determined using Colby’s formula [R. S. Colby, Weeds 15, 20-22 (1967)] and compared with the observed efficacies.

\[ E_{\text{expected}} = E_{\text{actual}} \times \text{Colby's formula} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times (a + b) - ab}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times a}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times b}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times (a + b) - ab}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times a}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times b}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times (a + b) - ab}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times a}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times b}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times (a + b) - ab}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times a}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times b}{a + b} \]

\[ E_{\text{expected}} = \frac{E_{\text{actual}} \times (a + b) - ab}{a + b} \]
USE EXAMPLE 1

Activity Against Mildew of Wheat Caused by *Erysiphe* [syn. *Blumeria*] *graminis* forma specialis. *tritici*

[0086] Leaves of wheat seedlings of the cultivar “Kanzler” grown in pots were sprayed to runoff point with an aqueous preparation of active compound which had been prepared from a stock solution comprising 10% of active compound, 85% of cyclohexanone and 5% of emulsifier, and, 24 hours after the spray coating had dried on, the leaves were dusted with spores of mildew of wheat (*Erysiphe* [syn. *Blumeria*] *graminis* forma specialis. *tritici*). The test plants were then placed in a greenhouse at 20-24°C and 60-90% relative atmospheric humidity. After 7 days, the extent of the development of the mildew was determined visually in % infection of the entire leaf area.

[0087] The visually determined values for the percentage of diseased leaf areas were converted into efficacies as % of the untreated control. An efficacy of 0 means the same disease level as in the untreated control, an efficacy of 100 means a disease level of 0%. The expected efficacies for the active compound combinations were determined using Colby’s formula mentioned above and compared with the observed efficacies.

### TABLE 1

<table>
<thead>
<tr>
<th>Active compound</th>
<th>Concentration of active compound in the spray liquor in ppm</th>
<th>Efficacy in % of the untreated control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0 (untreated)</td>
<td>0</td>
</tr>
<tr>
<td>Compound I = prothioconazole</td>
<td>4</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>0</td>
</tr>
<tr>
<td>Compound II = trifloxystrobin</td>
<td>4</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>0</td>
</tr>
<tr>
<td>Compound III = picoxystrobin</td>
<td>0.25</td>
<td>11</td>
</tr>
<tr>
<td>Compound IV = pyraclostrobin</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0</td>
</tr>
</tbody>
</table>

[0088]

### TABLE 2

<table>
<thead>
<tr>
<th>Combinations according to the invention</th>
<th>Observed efficacy</th>
<th>Calculated efficacy*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin</td>
<td>33</td>
<td>22</td>
</tr>
<tr>
<td>0.015 + 0.25 ppm Mixture 1:16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin</td>
<td>94</td>
<td>83</td>
</tr>
<tr>
<td>1:4 ppm Mixture 1:4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin</td>
<td>56</td>
<td>44</td>
</tr>
<tr>
<td>0.25 + 1 ppm Mixture 1:4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>0.25 + 0.05 ppm Mixture 4:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>4 + 0.25 ppm Mixture 16:1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[0089] The test results show that in all mixing ratios the observed efficacy is higher than the efficacy calculated beforehand using Colby’s formula (from Synerg 171. XLS).

[0090] Use example 2: Curative activity against brown rust of wheat caused by *Puccinia recondita*

[0091] Leaves of wheat seedlings of the cultivar “Kanzler” grown in pots were dusted with spores of brown rust (*Puccinia recondita*). The pots were then placed in a chamber with high atmospheric humidity (90-95%), at 20-22°C, for 24 hours. During this time, the spores germinated and the germinal tubes penetrated into the leaf tissue. The next day, the infected plants were sprayed to runoff point with an aqueous formulation of active compound prepared from a stock solution comprising 10% of active compound, 85% of cyclohexanone and 5% of emulsifier. After the spray coating had dried on, the test plants were cultivated in a greenhouse at 20-22°C and 65-70% relative atmospheric humidity for 7 days. Thereafter, the extent of the rust fungus development on the leaves was determined.

[0092] The visually determined values for the percentage of diseased leaf areas were converted into efficacies as % of the untreated control. An efficacy of 0 means the same disease level as in the untreated control, an efficacy of 100 means a disease level of 0%. The expected efficacies for the combinations of active compounds were determined using Colby’s formula mentioned above and compared with the observed efficacies.

### TABLE 3

<table>
<thead>
<tr>
<th>Active compound</th>
<th>Concentration of active compound in the spray liquor in ppm</th>
<th>Efficacy in % of the untreated control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (untreated)</td>
<td>(90% infected)</td>
<td>0</td>
</tr>
<tr>
<td>Compound I = prothioconazole</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.006</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE 3-continued

<table>
<thead>
<tr>
<th>Active compound</th>
<th>Concentration of active compound in the spray liquor in ppm</th>
<th>Efficacy in % of the untreated control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound II = trifloxystrobin</td>
<td>0.25, 0.06</td>
<td>0, 0</td>
</tr>
<tr>
<td>Compound III = picoxystrobin</td>
<td>1, 0.25, 0.06</td>
<td>33, 0, 0</td>
</tr>
<tr>
<td>Compound IV = picoxystrobin</td>
<td>0.25, 0.06</td>
<td>0, 0</td>
</tr>
</tbody>
</table>

[0093]

TABLE 4

<table>
<thead>
<tr>
<th>Combinations according to the invention</th>
<th>Observed efficacy</th>
<th>Calculated efficacy*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin 0.015 or 0.25 ppm Mixture 1:16</td>
<td>22 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin 0.06 or 0.25 ppm Mixture 1:4</td>
<td>22 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin 0.25 or 0.25 ppm Mixture 4:1</td>
<td>67 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound II = trifloxystrobin 0.25 or 0.06 ppm Mixture 4:1</td>
<td>11 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound III = picoxystrobin 0.06 or 1 ppm Mixture 1:16</td>
<td>11 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound III = picoxystrobin 0.06 or 0.25 ppm Mixture 1:4</td>
<td>78 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound III = picoxystrobin 0.25 or 0.25 ppm Mixture 4:1</td>
<td>78 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound III = picoxystrobin 0.25 or 0.06 ppm Mixture 4:1</td>
<td>44 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound IV = pymeclobutiol 0.015 or 0.25 ppm Mixture 1:16</td>
<td>94 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound IV = pymeclobutiol 0.06 or 0.25 ppm Mixture 1:4</td>
<td>89 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound IV = pymeclobutiol 0.25 or 0.25 ppm Mixture 4:1</td>
<td>22 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound IV = pymeclobutiol 0.25 or 0.06 ppm Mixture 4:1</td>
<td>22 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound IV = pymeclobutiol 0.25 or 0.06 ppm Mixture 4:1</td>
<td>89 or 0</td>
<td></td>
</tr>
<tr>
<td>Compound I = prothioconazole + Compound IV = pymeclobutiol 0.015 or 0.25 ppm Mixture 1:16</td>
<td>94 or 0</td>
<td></td>
</tr>
</tbody>
</table>

*efficacy calculated using Colby's formula

[0094] The test results show that in all mixing ratios the observed efficacy is higher than the efficacy calculated beforehand using Colby's formula (from Synerg 171. XLS).

1. A fungicidal mixture, comprising (1) 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione (prothioconazole) of the formula I or its salts or adducts

![Image of prothioconazole molecule]

and at least one further fungicidal compound or its salts or adducts, selected from the group consisting of

2. Trifloxystrobin of the formula II

![Image of trifloxystrobin molecule]

and

3. Picoxystrobin of the formula III

![Image of picoxystrobin molecule]

and

4. Pyraclostrobin of the formula IV

![Image of pyraclostrobin molecule]
and

(5) dimoxystrobin of the formula V

\[
\text{Dimoxystrobin}
\]

and

(6) a strobilurin derivative of the formula VI

\[
\text{Trifloxystrobin}
\]

in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, comprising prothioconazole of the formula I and trifloxystrobin of the formula II.

3. A fungicidal mixture as claimed in claim 1, comprising prothioconazole of the formula I and picoxystrobin of the formula III.

4. A fungicidal mixture as claimed in claim 1, comprising prothioconazole of the formula I and pyraclostrobin of the formula IV.

5. A fungicidal mixture as claimed in claim 1, comprising prothioconazole of the formula I and dimoxystrobin of the formula V.

6. A fungicidal mixture as claimed in claim 1, comprising prothioconazole of the formula I and the strobilurin derivative of the formula VI.

7. A fungicidal mixture as claimed in claim 1, wherein the weight ratio of prothioconazole of the formula I to trifloxystrobin of the formula II is from 20:1 to 1:20, picoxystrobin of the formula III is from 20:1 to 1:20, pyraclostrobin of the formula IV is from 20:1 to 1:20, dimoxystrobin of the formula V is from 20:1 to 1:20 and the strobilurin derivative of the formula VI is from 20:1 to 1:20.

8. A method for controlling harmful fungi, which comprises treating the harmful fungi, their habitat or the plants, seeds, soils, areas, materials or spaces to be kept free from them with an anti-fungal effective amount of a compound of formula I or a salt or adduct thereof.
9. A method as claimed in claim 8, wherein the compound of the formula I as set forth in claim 1 and at least one compound of the formula II, III, IV, V or VI as set forth in claim 1 are applied simultaneously, that is together or separately, or in succession.

10. (canceled)

11. A fungicidal composition, comprising the fungicidal mixture as claimed in claim 1 and a solid or liquid carrier.

12. A method as claimed in claim 8, wherein the compounds are applied to agricultural crop areas in a total amount of from 0.1 to 8 kg/ha.

13. A fungicidal kit for controlling harmful fungi comprising, in separate containers, a compound of formula I or a salt or adduct thereof, and at least one compound of formula II, IV, IV or V

(3) piclouxystrobin of the formula III

(4) pyraclostrobin of the formula IV

(5) dimoxystrobin of the formula V

* * * * *