I/We being the person(s) identified below as the Applicant(s), request the grant of a patent to the person(s) identified below as the Nominated Person(s), for an invention described in the accompanying standard complete specification.

Full application details follow:

[71/70] Applicant(s)/Nominated Person(s):
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[54] Invention Title:
Mixed agrochemical combination

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Basic Convention Application(s) Details:

91 15397 France FR 6 December 1991

DATED this SECOND day of DECEMBER 1992

[Signature]

a member of the firm of DAVIES COLLISON CAVE for and on behalf of the applicant(s)
We, Rhone-Poulenc Agrochimie, the applicant/Nominated Person in respect of Application No. 29789/92 state the following:-

The Nominated Person is entitled to the grant of the patent because the Nominated Person would, on the grant of a patent for the invention to the inventors, be entitled to have the patent assigned to the Nominated Person.

The Nominated Person is entitled to claim priority from the basic application listed on the patent request because the Nominated Person made the basic application, and because that application was the first application made in a Convention country in respect of the invention.

DATED this THIRTY FIRST day of DECEMBER 1992

[Signature]

a member of the firm of DAVIES COLLISON CAVE for and on behalf of the applicant(s)

(DCC ref: 1553825)
1. Agrochemical combination for the protection of plants against plant diseases and plant-eating insects, characterised in that it comprises at least an effective quantity of a benzylidene azolylmethylcycloalkane fungicide and at least an effective quantity of the insecticide imidacloprid.

6. Process for the treatment of plants in order to protect them against diseases and plant-eating insects, characterised in that an effective quantity of a benzylidene azolylmethylcycloalkane fungicide and an effective quantity of imidacloprid is applied.
NAME OF APPLICANT(S):

Rhone-Poulenc Agrochimie

ADDRESS FOR SERVICE:

DAVIES COLLISON CAVE
Patent Attorneys
1 Little Collins Street, Melbourne, 3000.

INVENTION TITLE:

Mixed agrochemical combination

The following statement is a full description of this invention, including the best method of performing it known to me/us:-
The present invention relates to new agrochemical combinations for the protection of plants comprising both an active fungicidal material and an active insecticidal material as well as a process for the treatment of plants using these combinations.

In this specification, including the accompanying claims it is to be understood that the term "plant" embraces an entire plant, a part of a plant or plant propagation material, especially a seed.

More particularly, the subject of the invention is an agrochemical combination for the protection of plants against diseases and plant-eating insects, characterised in that it comprises at least an effective quantity of a benzylidene azolylmethylcycloalkane fungicide and at least an effective quantity of the insecticide imidacloprid.

There may be cited, as the benzylidene azolylmethylcycloalkane fungicide, in particular those described in the European Patent Application 0,378,953, and preferably 2-(4-chlorobenzylidene)-5,5-dimethyl-1-(1H-1,2,4-triazol-1-ylmethyl)-1-cyclopentanol or triticonazole and 2-(4-chlorobenzylidene)-1-(1H-1,2,4-triazol-1-ylmethyl)-1-cyclohexanol.

Imidacloprid is the common name for 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidene-amine described for its insecticidal properties, especially in the proceedings "Pests and Diseases", Brighton Crop Protection Conference, 1990, p. 21.

It has been found that combinations based on these
two types of products are particularly advantageous for the protection of plants against diseases and plant-eating insects.

The combinations according to the invention can be preferably used for the protection of seeds or in soil treatment.

The fungicide is preferably used at a dose of from 2.5 to 250 g per quintal and the insecticide is preferably used at a dose of from 25 to 2000 g per quintal of seed.

A further subject of the invention is compositions based on each of the two active materials.

The invention additionally comprises a process for the treatment of plants for the protection of plants against diseases and plant-eating insects, characterised in that a combination of the two active materials is applied either simultaneously or successively so as to have the conjugate effect.

The following examples are given in order to illustrate the combinations, compositions and treatment according to the invention.

EXAMPLE

Wheat seeds of the Talent variety were treated with:
- on the one hand, triticonazole alone, at doses of 60, 120 and 180 g of active material per quintal (a.m.g./q),
- on the other hand, imidacloprid alone, at doses of 200 and 400 g (a.m.g./q),
- finally, triticonazole + imidacloprid mixtures, each active material being individually at each of the doses indicated above.

An aqueous suspension containing 200 g/l of
triticonazole is prepared, containing:

- 40% aqueous solution of ethoxylated tristyryl phenol in the potassium phosphate form (dispersing agent). 30 g

- oxyethylenated nonylphenol containing 10 mol of ethylene oxide (wetting agent) 10 g
- propylene glycol 50 g
- polysaccharide (Rhodopol 23) 3 g
- 1,2-benzisothiazolin-3-one (biocide) 1.5 g
- silicone antifoam 3 g
- water q.s. 1000 ml

An imidacloprid composition is used in the form of a commercial formulation of a 70% aqueous suspension of active material, sold under the trade name Gaucho by the Company Bayer.

The two compositions are applied to the seeds by treatment in a "Hege bowl" apparatus for 30 seconds. The seeds are sown in a peat/pozzuolana (1:1) substrate contained in 10 cm x 10 cm pots, at a ratio of 10 seeds per pot (there are 4 pots per repetition). Untreated seeds were sown under the same conditions. 4 weeks after sowing, the seedlings are infected with a suspension of spores of Puccinia recondita and infested with a population of Aphis sp.

Two weeks after contamination, visual inspection is carried out of the activity both against Puccinia recondita and Aphis sp, by comparison with control plants which carry more than 100 Aphis per plant and more than 50 rust pustules per leaf.
The results observed are recorded in the table below:

<table>
<thead>
<tr>
<th>Active material (a.m.g./q)</th>
<th>% effectiveness on Puccinia recondita</th>
<th>% effectiveness on Aphis sp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triticonazole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>180</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>more than 90 %</td>
</tr>
<tr>
<td>400</td>
<td>0</td>
<td>more than 90 %</td>
</tr>
<tr>
<td>Triticonazole + imidacloprid No.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 + 200</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>60 + 400</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>120 + 200</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>120 + 400</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>180 + 200</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>180 + 400</td>
<td>6</td>
<td>100</td>
</tr>
</tbody>
</table>

Moreover, no phytotoxicity phenomenon was observed.

These results clearly show that the combination of the two materials makes it possible to effectively control both brown rust disease on the wheat due to *Puccinia recondita* and infestation with an insect *Aphis sp*.

Of course, this example is not limiting and many
other diseases and infestations by insects can be treated with the combinations and compositions according to the invention.

This example well illustrates the value of the combinations according to the invention, namely in being able to combine in a single treatment, preferably a seed treatment, the excellent activity of the two active materials, one an insecticide and the other a fungicide, without any harmful interplay.

For practical use, the combinations according to the invention can be used by using compositions containing one or the other of the active materials or both together. In each composition, the active materials are generally used in combination with a solid or liquid vehicle which can be used in agriculture and, optionally, at least one surface-active agent.

For their practical use, the constituents of the combination according to the invention are rarely used on their own. Most often they form part of compositions. These compositions, which can be used for the protection of plants against fungal diseases and/or against plant-eating insects or in plant growth regulating compositions, contain, as active material, at least one of the constituents of the combination according to the invention as described above in combination with solid or liquid vehicles which are acceptable in agriculture, and/or surface-active agents which are also acceptable in agriculture. In particular, the usual inert vehicles and the usual surface-active agents can be used.

These compositions generally contain between 0.5 and 95% of combination according to the invention.
The term "vehicle", in the present account, means a natural or synthetic organic or inorganic material with which the active material is combined in order to facilitate its application to the plant, to seeds or to the soil. The vehicle is therefore generally inert and it has to be acceptable in agriculture, especially to the treated plant. The vehicle can be solid (clays, natural or synthetic silicates, silica, resins, waxes, solid fertilisers, and the like) or liquid (water, alcohol, ketones, petroleum fractions, aromatic or aliphatic hydrocarbons, chlorinated hydrocarbons, liquefied gases, and the like).

The surface-active agent can be an emulsifying, dispersing or wetting agent of ionic or nonionic type. There may be cited, for example, salts of poly(acrylic acids), salts of lignosulphonic acids, salts of phenolsulphonic or naphthalenesulphonic acids, polycondensates of ethylene oxide with fatty alcohols or fatty acids or fatty amines, substituted phenols (especially alkylphenols or arylphenols), salts of esters of sulphosuccinic acids, derivatives of taurine (especially alkyltaurates), and phosphoric esters of polyoxyethylenated alcohols or phenols. The presence of at least one surface-active agent is generally indispensable where the active material and/or the inert vehicle are not soluble in water and where the vector agent of the application is water.

These compositions can also contain all kinds of other ingredients such as, for example, protective colloids, adhesives, thickening agents, thixotropic agents, penetration agents, stabilising agents, sequestering agents and the like, as well as other known active materials possessing pesticidal
properties (especially insecticides or fungicides) or possessing properties which promote plant growth (especially fertilisers) or possessing properties which regulate plant growth. More generally, the compounds according to the invention can be used in combination with any of the solid or liquid additives which correspond to the usual formulating techniques.

For their application, the constituents of the combination are thus often in the form of compositions, which are themselves in fairly diverse solid or liquid forms.

There may be mentioned, as solid composition forms, powders for dusting or dispersing (containing the combination according to the invention at a content of up to 100%) and granules, especially those obtained by extrusion, by compacting, by impregnation of a granulated vehicle, or by granulation from a powder (the content of the combination according to the invention in these granules being between 1 and 80% for the latter cases).

According to one example of a granular composition, the following constituents are used:

**Example G**

- combination No.3 50 g
- epichlorohydin 2.5 g
- cetyl polyglycol ether 2.5 g
- polyethylene glycol 35 g
- kaolin (particle size: 0.3 to 0.8 mm) 910 g

In this particular case, the active materials are mixed with the epichlorohydrin and the mixture is dissolved
with 60 g of acetone; polyethylene glycol and cetyl polyglycol ether are then added. The solution obtained is sprayed over the kaolin and the acetone is then evaporated off under vacuum. Such a microgranule is used advantageously for controlling soil fungi.

The compounds of formula (I) can also be used in the powder form for dusting; it is also possible to use a composition comprising 50 g of active material and 950 g of talc; it is also possible to use a composition comprising 20 g of active material, 10 g of finely divided silica and 970 g of talc; these constituents are mixed and milled and the mixture is applied by dusting.

There may be cited, as liquid composition forms or as forms intended to constitute liquid compositions during application, solutions, in particular water-soluble concentrates, emulsifiable concentrates, emulsions, suspension concentrates, aerosols, wettable powders (or sprayable powder) or pastes.

The emulsifiable or soluble concentrates most often comprise 10 to 80 % of active material, while the ready-to-apply solutions or emulsions contain 0.01 to 20 % of active material.

For example, in addition to the solvent, the emulsifiable concentrates can contain, when this is necessary, 2 to 20 % of suitable additives such as the stabilising agents, surface-active agents, penetration agents, corrosion inhibitors, dyes or adhesives mentioned above.

By way of example, the composition of several concentrates will now be given:
EC Example 1

- combination 1 400 g/l
  - alkaline dodecylbenzenesulphonate 24 g/l
  - oxyethylenated nonylphenol containing 10 molecules of ethylene oxide 16 g/l
  - cyclohexanone 200 g/l
  - aromatic solvent qs 1 litre

According to another emulsifiable concentrate formula, there are used:

EC Example 2

- combination 2 250 g
  - epoxidised vegetable oil 25 g
  - mixture of alkylarylsulphonate and of ether of polyglycol and fatty alcohols 100 g
  - dimethylformamide 50 g
  - xylene 575 g

It is possible, by diluting these concentrates with water, to obtain emulsions of any desired concentration particularly suitable for application to leaves.

The suspension concentrates, which can also be applied by spraying, are prepared so as to produce a stable fluid product which does not settle out and they generally contain from 10 to 75 % of active material, from 0.5 to 15 % of surface-active agents, from 0.1 to 10 % of thixotropic agents, from 0 to 10 % of suitable additives, such as antifoaming agents, corrosion inhibitors, stabilising agents, penetration agents and adhesives and, as vehicle, water or an organic liquid in which the active material has little or no solubility: certain solid organic materials or inorganic salts.
can be dissolved in the vehicle to help in preventing sedimentation or as antifreeze for water.

Wettable powders (or sprayable powders) are generally prepared so that they contain 20 to 95 % of active material, and they generally contain, in addition to the solid vehicle, from 0 to 5 % of a wetting agent, from 3 to 10 % of a dispersing agent and, when necessary, from 0 to 10 % of one or more stabilising agents and/or other additives, such as penetration agents, adhesives, or anticaking agents, dyes, and the like.

By way of example, various wettable powder compositions will now be given:

WP Example 1:
- combination No. 3 50 %
  - calcium lignosulphonate (deflocculating agent) 5 %
  - isopropynaphthalenesulphonate (anionic wetting agent) 1 %
  - anticaking silica 5 %
  - kaolin (filler) 39 %

Another 70 % sprayable powder composition uses the following constituents:

WP Example 2:
- combination No. 4 700 g
  - sodium dibutynaphthylsulphonate 50 g
  - condensation product, in proportions of 3/2/1, of naphthalenesulphonic acid, phenolsulphonic acid and formaldehyde 30 g
  - kaolin 100 g
Another 40 % sprayable powder composition uses the following constituents:

WP Example 3:

- combination No. 5 400 g
- sodium lignosulphonate 50 g
- sodium dibutyl-naphthalenesulphonate 10 g
- silica 540 g

Another 25 % sprayable powder composition uses the following constituents:

WP Example 4:

- combination No. 1 250 g
- calcium lignosulphonate 45 g
- equal weight mixture of Champagne chalk and hydroxyethylcellulose 19 g
- sodium dibutyl-naphthalenesulphonate 15 g
- silica 195 g
- Champagne chalk 195 g
- kaolin 281 g

Another 25 % sprayable powder composition uses the following constituents:

WP Example 5:

- combination No. 2 250 g
- isooctylphenoxy-polyoxyethylene-ethanol 25 g
- equal weight mixture of Champagne chalk and hydroxyethylcellulose 17 g
- sodium aluminosilicate 543 g
- kieselguhr 165 g

Another 10 % sprayable powder composition uses the...
following constituents:

WP Example 6:
- combination No. 3 100 g
- mixture of sodium salts of sulphates 30 g
  of saturated fatty acids 30 g
- condensation product of naphthalene-
  sulphonate acid and formaldehyde 50 g
- kaolin 820 g

In order to obtain these sprayable powders or
wettable powders, the active materials are intimately mixed in
suitable mixers with additional substances and the mixture is
milled in mills or other suitable grinders. Sprayable powders
are thereby obtained whose wettability and suspensibility are
advantageous; they can be suspended in water at any desired
concentration and these suspensions can be used very
advantageously in particular for application to plant leaves.

In place of wettable powders, it is possible to
produce pastes. The conditions and methods for producing and
using these pastes are similar to those for wettable powders or
sprayable powders.

As has already been said, aqueous dispersions and
emulsions, for example the compositions obtained by diluting a
wettable powder or an emulsifiable concentrate using water
according to the invention, are included within the general
scope of the present invention. The emulsions can be of water-
in-oil or oil-in-water type and they can have a thick
consistency like that of a "mayonnaise".

In the case where the combinations according to the
invention are used as fungicides, the usage doses can vary
within wide limits, especially depending on the virulence of the fungi and the climatic conditions.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Agrochemical combination for the protection of plants against plant diseases and plant-eating insects, characterised in that it comprises at least an effective quantity of a benzylidene azolymethylcycloalkane fungicide and at least an effective quantity of the insecticide imidacloprid.

2. Agrochemical combination according to Claim 1, characterised in that the benzylidene azolymethylcycloalkane fungicide is triticonazole.

3. Combination according to either of Claims 1 and 2, characterised in that each of the active materials is mixed with an inert vehicle and optionally at least one surface-active agent.

4. Agrochemical composition for the protection of plants against plant diseases and plant-eating insects, characterised in that it comprises an agrochemical combination based on a benzylidene azolymethylcycloalkane fungicide and the insecticide imidacloprid in association with a diluent or carrier and, optionally, a surface active agent.

5. Agrochemical composition according to Claim 4, characterised in that the benzylidene azolymethylcycloalkane fungicide is triticonazole.

6. Process for the treatment of plants in order to protect them against diseases and plant-eating insects, characterised in that an effective quantity of a benzylidene azolymethylcycloalkane fungicide and an effective quantity of imidacloprid is applied.

7. Process according to Claim 6, characterised in that the two active materials are applied simultaneously.
8. Process according to Claim 7, characterised in that the two active materials are applied successively and conjugately.

9. Process according to one of Claims 6 to 8, characterised in that at least one of the two active materials is applied in seed treatment.

10. Process according to one of Claims 6 to 9, characterised in that at least one of the two active materials is applied in soil treatment.

11. Process according to one of Claims 6 to 10, characterised in that triticonazole is applied in a dose of from 2.5 to 250 g per quintal of seed.

12. Process according to one of Claims 6 to 11, characterised in that imidacloprid is applied in a dose of from 25 to 2000 g per quintal of seed.

13. Process according to one of Claims 1 to 12, characterised in that the plant treated is a cereal.
14. A composition according to claim 1, or claim 4, or a process according to claim 7, substantially as hereinbefore described with reference to the Examples.

15. The steps, features, compositions and compounds disclosed herein or referred to or indicated in the specification and/or claims of this application, individually or collectively, and any and all combinations of any two or more of said steps or features.

DATED this SECOND day of DECEMBER 1992

Rhone-Poulenc Agrochimie

by DAVIES COLLISON CAVE
Patent Attorneys for the applicant(s)