

(CONVENTION. By one or more persons and/or a Comp.

628675

8/4

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here  
insert (in  
full) Name  
or Names of  
Applicant or  
Applicants,  
followed by  
Address(es).

(1) BASF AKTIENGESELLSCHAFT  
We of D-6700 Ludwigshafen, Federal Republic of Germany

(2) Here  
insert Title  
of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)  
FUNGICIDAL MIXTURE

which is described in the accompanying complete specification. This application is a  
Convention application and is based on the application numbered (3)

P39 35 113.0

for a patent or similar protection made in (4) Federal Republic of Germany  
on 21st October 1989

(3) Here insert  
number(s)  
of basic  
application(s).

(4) Here insert  
Name of basic  
Country or  
Countries, and  
basic date or  
dates.

Our address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS  
290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this 18th day of October 1990

(5) Signature(s) of  
Applicant(s)  
or  
Seal of  
Company and  
Signatures of  
its Officers as  
prescribed by  
its Articles of  
Association.

by (5) BASF AKTIENGESELLSCHAFT  
..... Louis C. Gebhardt  
..... Registered Patent Attorney

To: THE COMMISSIONER OF PATENTS.

(CONVENTION. Company.)

## COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1962

DECLARATION IN SUPPORT OF A CONVENTION  
APPLICATION FOR A PATENT OR PATENT OF ADDITION(1) Here  
insert (in  
full) Name of  
Company.In support of the Convention Application made by<sup>(1)</sup>BASF Aktiengesellschaft, a German Joint Stock Company of  
6700 Ludwigshafen, Federal Republic of Germany;(2) Here  
insert title  
of Invention.(hereinafter referred to as the applicant) for a Patent  
for an invention entitled:<sup>(2)</sup>(3) Here  
insert full Name  
and Address  
of Company  
official  
authorized  
to make  
declaration.

Fungicidal mixture

(3)  We, GUNTHER WELZEL and PETER BARZ, citizens of the  
Federal Republic of Germany, residing, respectively, at  
Auf dem Koeppel, 6702 Bad Duerkheim; and 20 Hochfeldstrasse,  
6700 Ludwigshafen; Federal Republic of Germany;

do solemnly and sincerely declare as follows:

We are

1.  authorised by the applicant for the patent  
to make this declaration on its behalf.2. The basic application as defined by Section 141 of the Act was  
made in<sup>(4)</sup> the Federal Republic of Germany under No.(4) Here  
insert basic  
Country or  
Countries  
followed by  
date or dates  
and basic  
Applicant or  
Applicants.P 39 35 113.0 on the 21st day of October 1989,  
by. BASF Aktiengesellschaft

xxby

xx

19

(5) Here  
insert (in  
full) Name  
and Address  
of Actual  
Inventor or  
Inventors.3. (5) RAINER SEELE, FRIEDRICH LOECHER, REINHOLD SAUR,  
EBERHARD AMMERMANN, GISELA LORENZ,  
citizens of the Federal Republic of Germany, residing,  
respectively, at3 Leiblstrasse, 6701 Fussgoenheim;  
34 Kropsburgstrasse, 6703 Limburgerhof;  
9 Koenigsberger Strasse, 6737 Boehl-Iggelheim;  
3 Sachsenstrasse, 6700 Ludwigshafen;  
13 Erlenweg, 6730 Neustadt; Federal Republic of Germany;xxis/are the actual inventors of the invention and the facts upon which the applicant  
is entitled to make the application are as follow:

The applicant is the assignee of. the invention from the said

RAINER SEELE, FRIEDRICH LOECHER, REINHOLD SAUR,  
EBERHARD AMMERMANN, GISELA LORENZ.4. The basic application referred to in paragraph 2 of this Declaration  
was. the first application made in a Convention country in  
respect of the invention the subject of the application.

DECLARED at 6700 Ludwigshafen, Federal Republic of Germany

this. 10 th day of October 1990

(6) Signature.

(6) BASF Aktiengesellschaft

(12) PATENT ABRIDGMENT (11) Document No. AU-B-64785/90  
 (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 628675

(54) Title  
**FUNGICIDAL MIXTURE**

International Patent Classification(s)  
 (51)<sup>5</sup> A01N 043/653 A01N 043/40 A01N 043/84

(21) Application No. : 64785/90 (22) Application Date : 19.10.90

(30) Priority Data

(31) Number 3935113 (32) Date 21.10.89 (33) Country DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date : 26.04.91

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(71) Applicant(s)  
**BASF AKTIENGESELLSCHAFT**

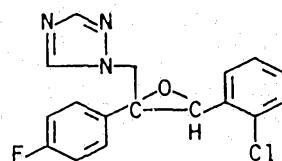
(72) Inventor(s)  
**RAINER SEELE; FRIEDRICH LOECHER; REINHOLD SAUR; EBERHARD AMMERMANN; GISELA LORENZ**

(74) Attorney or Agent  
**WATERMARK PATENT & TRADEMARK ATTORNEYS, Locked Bag 5, HAWTHORN VIC 3122**

(57) Claim

1. A fungicidal agent containing a fungicidally effective amount of a mixture consisting of

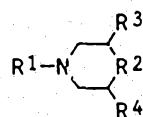
a) 2-(1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-(2-chlorophenyl)-oxirane of the formula I



I

and

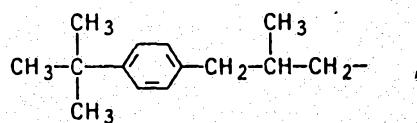
b) a heterocyclic compound of the formula II



II

where

R1 = tridecyl (CH<sub>3</sub>-C<sub>12</sub>H<sub>24</sub>-) or the radical



R2 = CH<sub>2</sub> or O

R<sup>3</sup>, R<sup>4</sup> = methyl or H, or a plant-tolerated salt or metal complex thereof.

628675

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

## COMPLETE SPECIFICATION

(ORIGINAL)

Application Number:

Lodged:

Class

Int. Class

Complete Specification Lodged:

Accepted:

Published:

Priority :

Related Art :

Name of Applicant : BASF AKTIENGESELLSCHAFT

Address of Applicant : D-6700 Ludwigshafen, Federal Republic of Germany

Actual Inventor : RAINER SEELE, FRIEDRICH LOECHER, REINHOLD SAUR, EBERHARD AMMERMANN and GISELA LORENZ

Address for Service : WATERMARK PATENT & TRADEMARK ATTORNEYS,  
LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA

Complete Specification for the invention entitled:

FUNGICIDAL MIXTURE

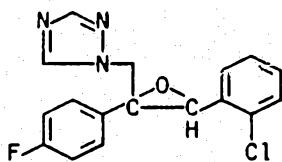
The following statement is a full description of this invention, including the best method of performing it known to :-

us

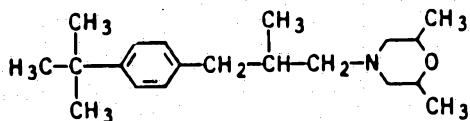
Fungicidal mixture

The present invention relates to fungicidal mixtures having a synergistic fungicidal action and methods for controlling fungi with these mixtures.

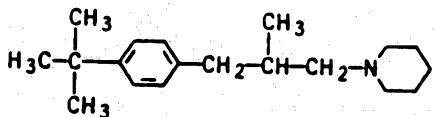
5 It is known that 2-(1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-(2-chlorophenyl)-oxirane of the formula



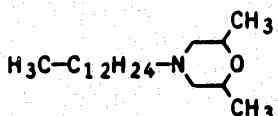
or one of its salts can be used as a fungicide (EP 196 038). It is also known that the active ingredients 10 fenpropimorph, 4-[3-(4-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethylmorpholine of the formula



or its salts, fenpropidine, N-[3-(4-tert-butylphenyl)-2-methylpropyl]-piperidine of the formula



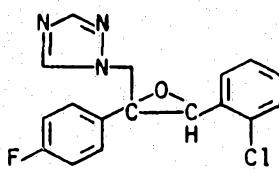
or its salts, or the active ingredient tridemorph, N-15 tridecyl-2,6-dimethylmorpholine of the formula



or its salts can be used as fungicides (DE-A 27 52 096, 27 52 135 and 11 65 930).

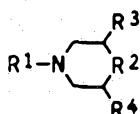
We have found that a mixture of

a) 2-(1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-(2-chlorophenyl)-oxirane of the formula I



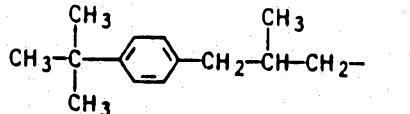
and

b) a heterocyclic compound of the formula II



where

R<sup>1</sup> is tridecyl (CH<sub>3</sub>-C<sub>12</sub>H<sub>24</sub>-) or the radical



R<sup>2</sup> is CH<sub>2</sub> or O and

R<sup>3</sup> and R<sup>4</sup> are each methyl or H,  
or a plant-tolerated salt or metal complex thereof  
has a synergistic fungicidal action. The mixing  
ratio (weight ratio) of the compounds a) and b) is  
chosen to give a synergistic fungicidal action, for  
example compound a) and compound b) in a ratio of  
from 5 : 1 to 1 : 5, in particular from 3 : 1 to  
1 : 3, preferably from 2 : 1 to 1 : 2.

2-(1,2,4-Triazol-1-ylmethyl)-2-(4-fluorophenyl)-  
3-(2-chlorophenyl)-oxirane, component a), may occur in  
four stereoisomeric forms which have different fungicidal  
activities. The two cis-isomers, ie. the enantiomers in  
which the triazolylmethyl group and the 2-chlorophenyl  
group are on the same side of the oxirane ring, are  
preferred. Fenpropimorph occurs in two enantiomeric  
forms, of which the (-)-enantiomer, which has an S-

5 configuration, is preferred as the active partner. The present invention includes mixtures of pure isomers of the compounds a) and b), in particular mixtures of a cis-enantiomer of 2-(1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-(2-chlorophenyl)-oxirane with the (-)cis-enantiomer of fenpropimorph.

10 The present invention also includes agents in which the active ingredient component a), 2-(1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-(2-chlorophenyl)-oxirane, is predominantly in the form of the two cis-enantiomers.

15 Salts are prepared by reaction with acids, for example halohydric acids, such as hydrofluoric acid, hydrochloric acid, hydrobromic acid or hydriodic acid, or sulfuric acid, phosphoric acid, nitric acid or organic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid, propionic acid, glycolic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic acid, formic acid, benzenesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, salicylic acid, p-aminosalicylic acid or 1,2-naphthalenedisulfonic acid.

20 Complexes can, if desired, contain only one component a) or one component b) or a plurality of components b). It is also possible to prepare metal complexes which contain both components a) and b) together in a mixed complex.

25 Metal complexes are prepared from the parent organic molecule and an inorganic or organic metal salt, for example the halides, nitrates, sulfates, phosphates, acetates, trifluoroacetates, trichloroacetates, propionates, tartrates, sulfonates, salicylates or benzoates of the metals of main group two, such as calcium or magnesium, and of main groups three and four, such as aluminum, tin or lead, and of subgroups one to eight, such as chromium, manganese, iron, cobalt, nickel, copper or zinc. The subgroup elements of the fourth period are

preferred. The metals may have their various valencies. The metal complexes may be mononuclear or polynuclear, ie. they may contain one or more organic molecular moieties as ligands, for example mixed complexes of 2-  
5 (1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-(2-chlorophenyl)-oxirane and fenpropimorph, fenpropidine or tridemorph.

10 In practice, it is advantageous to use the pure active ingredients a) and b) to which other agrochemical active substances, such as insecticides, acaricides, nematicides, herbicides, further fungicides, growth regulators and/or fertilizers, may also be added.

In general terms, the novel mixtures are extremely effective on a broad spectrum of phytopathogenic fungi, in particular those from the class consisting of the Ascomycetes and Basidiomycetes. Some of them have a systemic action and can be used as foliar and soil fungicides.

5

The fungicidal compounds are of particular interest for controlling a large number of fungi in various crops or their seeds, especially wheat, rye, barley, oats, rice, Indian corn, lawns, cotton, soybeans, coffee, sugar cane, fruit and ornamentals in horticulture and viticulture, and in 10 vegetables such as cucumbers, beans and cucurbits.

The novel compounds are particularly useful for controlling the following plant diseases:

- 15 Erysiphe graminis in cereals,  
Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits,  
Podosphaera leucotricha in apples,  
Uncinula necator in vines,  
Puccinia species in cereals,
- 20 Rhizoctonia solani in cotton,  
Ustilago species in cereals and sugar cane,  
Venturia inaequalis (scab) in apples,  
Helminthosporium species in cereals,  
Septoria nodorum in wheat,
- 25 Botrytis cinerea (gray mold) in strawberries and grapes,  
Cercospora arachidicola in groundnuts,  
Pseudocercosporella herpotrichoides in wheat and barley,  
Pyricularia oryzae in rice,  
Phytophthora infestans in potatoes and tomatoes,
- 30 Fusarium and Verticillium species in various plants,  
Plasmopara viticola in grapes,  
Alternaria species in fruit and vegetables.

The compounds are applied by spraying or dusting the plants with a fungicidally effective amount of the mixtures, or treating the seeds of the plants with the mixtures. They may be applied before or after infection of the plants or seeds by the fungi. Either the fungi themselves, or the plants, seed, materials or soil to be protected against fungus attack are treated with a fungicidally effective amount of the mixtures.

40

Active ingredients a) and b) may be applied one briefly after the other, the mixture thus being formed on the plant or seed.

The novel mixtures can be converted into conventional formulations such as solutions, emulsions, suspensions, dusts, powders, pastes and granules.

The application forms depend entirely on the purposes for which they are intended; they should at all events ensure a fine and uniform distribution

5 of the active ingredient. The formulations are produced in known manner, for example by extending the active ingredient with solvents and/or carriers, with or without the use of emulsifiers and dispersants; if water is used as solvent, it is also possible to employ other organic solvents as auxiliary solvents. Suitable auxiliaries for this purpose are solvents 10 such as aromatics (e.g., xylene), chlorinated aromatics (e.g., chlorobenzenes), paraffins (e.g., crude oil fractions), alcohols (e.g., methanol, butanol), ketones (e.g., cyclohexanone), amines (e.g., ethanolamine, dimethylformamide), and water; carriers such as ground natural minerals (e.g., kaolins, aluminas, talc and chalk) and ground 15 synthetic minerals (e.g., highly disperse silica and silicates); emulsifiers such as nonionic and anionic emulsifiers (e.g., polyoxyethylene fatty alcohol ethers, alkyl sulfonates and aryl sulfonates); and dispersants such as lignin, sulfite waste liquors and methylcellulose.

20 The fungicides generally contain from 0.1 to 95, and preferably from 0.5 to 90, wt% of active ingredient. The application rates are from 0.02 to 3 kg or more of active ingredient per hectare, depending on the type of effect desired. The novel mixtures may also be used for protecting materials (timber), e.g., against *Paecilomyces variotii*. When the mixtures 25 are used for treating seed, generally amounts of from 0.001 to 50, and preferably from 0.01 to 10, g per kg of seed are sufficient.

30 The agents and the ready-to-use formulations prepared from them, such as solutions, emulsions, suspensions, powders, dusts, pastes and granules, are applied in conventional manner, for example by spraying, atomizing, dusting, scattering, dressing or watering.

Examples of formulations are given below.

35 I. A solution of 90 parts by weight of a mixture of compound a) with fenpropimorph and 10 parts by weight of N-methyl- $\alpha$ -pyrrolidone, which is suitable for application in the form of very fine drops.

II. A mixture of 20 parts by weight of a mixture of compound a) with 40 fenpropidin, 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide and 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By finely dispersing the mixture in water, an aqueous dispersion is obtained.

III. A solution of 20 parts by weight of a mixture of compound a) with tridemorph, 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into water and finely 5 distributing it therein, an aqueous dispersion is obtained.

IV. A solution of 20 parts by weight of a mixture of compound a) with fenpropimorph, 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction having a boiling point between 210 and 280°C, and 10 10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the mixture into water and finely distributing it therein, an aqueous dispersion is obtained.

V. A hammer-milled mixture of 80 parts by weight of a mixture of compound a) with fenpropidin, 3 parts by weight of the sodium salt of diisobutyl-naphthalene- $\alpha$ -sulfonic acid, 10 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 7 parts by weight of powdered silica gel. By finely dispersing the mixture in water, a spray liquor is obtained.

VI. An intimate mixture of 3 parts by weight of a mixture of compound a) with tridemorph and 97 parts by weight of particulate kaolin. The dust 20 contains 3wt% of the active ingredient.

VII. An intimate mixture of 30 parts by weight of a mixture of compound a) with fenpropimorph, 92 parts by weight of powdered silica gel and 8 parts by weight of paraffin oil sprayed onto the surface of this silica 25 gel. This formulation of the active ingredient exhibits good adherence.

VIII. A stable aqueous dispersion of 40 parts by weight of a mixture of compound a) with fenpropidin, 10 parts of the sodium salt of a phenol-sulfonic acid-urea-formaldehyde condensate, 2 parts of silica gel and 48 parts of water, which dispersion can be further diluted.

IX. A stable oily dispersion of 20 parts by weight of a mixture of compound a) with tridemorph, 2 parts by weight of the calcium salt of do-decylbenzenesulfonic acid, 8 parts by weight of a fatty alcohol polyglycol ether, 2 parts by weight of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate and 68 parts by weight of a paraffinic mineral 30 oil.

In these application forms, the mixtures according to the invention may also be present together with other active ingredients, for example herbicides, insecticides, growth regulators, and fungicides, and may furthermore be mixed and applied together with fertilizers. Admixture with other fungicides frequently results in a greater fungicidal action spectrum.

## Use examples

## Example 1

## 5 Eradicative action on wheat mildew

Wheat plants of the "Kanzler" variety were inoculated at the 3-leaf stage with wheat mildew (*Erysiphe graminis* var. *tritici*), and treated, when the fungal attack had reached about 5%, with the active ingredients in the 10 stated concentrations. The amount of water employed was equivalent to 400 liters/ha. The plants were cultivated in the greenhouse for 20 days at from 18 to 22°C. The leaf area under attack was then assessed in percent.

These figures were converted to degrees of effectiveness. The degree of effectiveness which the active ingredient mixture should be expected to 15 have was determined in accordance with the Colby formula (Colby, S.R. "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds, 15, p. 20-22, 1967) and compared with the degrees of effectiveness actually observed.

20 The values for the fungicidal action vary from experiment to experiment, because the heaviness of the fungal attack on the plants varied in the individual experiments, thus giving different figures for the fungicidal action. For this reason, only results within the same experiment can be compared with each other.

25

$$\text{Colby formula } E = X + Y - \frac{X \cdot Y}{100}$$

30 E = expected degree of effectiveness, expressed in % of the untreated control, when active ingredients A and B are used in concentrations m and n

35 X = degree of effectiveness, expressed in % of the untreated control, when active ingredient A is used in a concentration of m

Y = degree of effectiveness, expressed in % of the untreated control, when active ingredient B is used in a concentration of n

40

Experiment 1: Erysiphe graminis Test (wheat); eradication

## Active ingredient

Active ingredient  
concentration in  
the spray liquor  
in %Degree of  
effectiveness  
in % of un-  
treated control

5

Control (untreated)

0

10

I Compound a) (prior art)

0.05

22

II fenpropimorph (prior art)

0.05

30

III fenpropidin (prior art)

0.05

33

15 IV tridemorph (prior art)

0.05

26

## Mixture according to the invention

20 I + II ratio

1 : 3

0.01 + 0.03

61

I + III ratio

1 : 3

0.01 + 0.03

62

I + IV ratio

1 : 3

0.01 + 0.03

58

These results show that 0.04% (0.01 + 0.03) of the mixture has a better  
 25 fungicidal action than 0.05% of the individual active ingredients.

30

35

890588

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O.Z. 0050/41191

Experiment 2: Erysiphe graminis Test (wheat); eradative

Active ingredient	Active ingredient concentration in the spray liquor in %	Degree of effectiveness in % of the untreated control
5		
Control (untreated)	-	0
10 I compound a) (prior art)	0.1	42
	0.05	15
15 II fenpropimorph (prior art)	0.1	72
	0.05	32
15		
Mixture according to the invention:	Observed degree of effectiveness	Calculated degree of effectiveness*)
20 I + II 0.05 + 0.05 ratio 1 : 1	65	42.2
25 I + II 0.1 + 0.1 ratio 1 : 1	100	83.8
25 I + II 0.1 + 0.05 ratio 2 : 1	82	60.6
30 I + II 0.05 + 0.1 ratio 1 : 2	95	73.2

\*) calculated according to the Colby formula

35

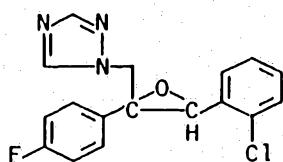
40

XXXXX THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A fungicidal agent containing a fungicidally effective amount of a mixture consisting of

5

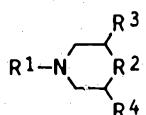
a) 2-(1,2,4-triazol-1-ylmethyl)-2-(4-fluorophenyl)-3-*o*-chlorophenyl-oxirane of the formula I



I

and

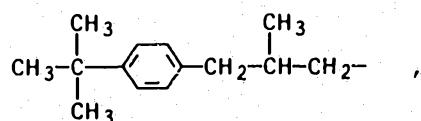
b) a heterocyclic compound of the formula II



II,

where

R1 = tridecyl ( $\text{CH}_3\text{--C}_{12}\text{H}_{24}\text{--}$ ) or the radical



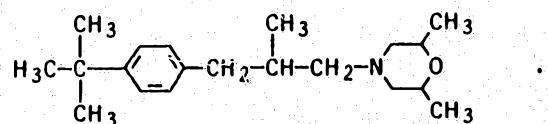
15

R2 =  $\text{CH}_2$  or 0

R3, R4 = methyl or H, or a plant-tolerated salt or metal complex thereof.

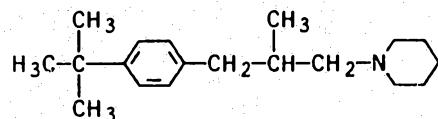
20

2. A fungicide as set forth in claim 1, containing as compound b) the compound 4-[3-(4-tert.-butylphenyl)-2-methylpropyl]-cis-2,6-dimethylmorpholine of the formula

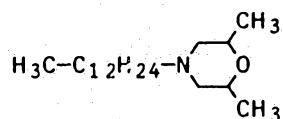


25

3. A fungicide as set forth in claim 1, containing as compound b) the compound of the formula



4. A fungicide as set forth in claim 1, containing as compound b) the  
5 compound N-tridecyl-cis-2,6-dimethylmorpholine of the formula



5. A process for combating fungi, wherein a fungicidally effective amount of a mixture as set forth in claim 1 is allowed to act on the fungi, or the materials, areas, plants or seed threatened by fungus attack.  
10  
6. A fungicide as set forth in claim 1, containing the compounds a) and b) in such an amount as to produce a synergistic fungicidal action.  
15 7. A fungicide as set forth in claim 1, containing the compounds a) and b) in a ratio of a : b of from 5 : 1 to 1 : 5.

20

DATED this 18th day of October 1990.

BASF AKTIENGESELLSCHAFT

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WATERMARK PATENT & TRADEMARK ATTORNEYS  
"THE ATRIUM"  
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30

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