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Fungicide mixtures based on pyridin carboxamides and benzimidazoles or the precursors thereof

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(54) Title: FUNGICIDE MIXTURES BASED ON PYRIDIN CARBOXAMIDES AND BENZIMIDAZOLES OR THE PRECURSORS THEREOF			
(54) Bezeichnung: FUNGIZIDE MISCHUNGEN AUF DER BASIS VON PYRIDINCARBOXAMIDEN UND BENZIMIDAZOLEN BZW. DEREN VORSTUFEN			
(57) Abstract			
<p>The invention relates to fungicide mixtures containing, as active components, a) an amide compound of formula (I) A-CO-NR¹R², wherein A represents an aryl group or an aromatic or non-aromatic, 5- or 6-structured heterocyclic compound having 1 to 3 heteroatoms selected from O, N, S; whereby the aryl group or the heterocyclic compound can optionally comprise 1, 2 or 3 substituents selected independently of one another from alkyl, halogen, CHF₂, CF₃, alkoxy, haloalkoxy, alkylthio, alkyl sulfinyl and alkyl sulfonyl; R¹ represents a hydrogen atom; R² represents a phenyl group or cycloalkyl group optionally containing 1, 2 or 3 substituents selected independently of one another from alkyl, alkenyl, alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkenyl, cycloalkyloxy, cycloalkenyloxy, phenyl and halogen, whereby the aliphatic and cycloaliphatic radicals can be partially or completely halogenated and/or the cycloaliphatic radicals can be substituted by 1 to 3 alkyl groups, whereby the phenyl group can contain 1 to 5 halogen atoms and/or 1 to 3 substituents selected independently of one another from alkyl, haloalkyl, alkoxy, haloalkylthio and haloalkylthio, and whereby the amidic phenyl group is optionally condensed with a saturated 5-structured ring which is optionally substituted by one or more alkyl groups and/or can comprise a heteroatom selected from O and S, and b) a fungicidal active substance from the class of benzimidazoles or the precursors (II) which release benzimidazoles. The active components are provided in a synergistically effective quantity.</p>			
(57) Zusammenfassung			
<p>Fungizide Mischungen, enthaltend als aktive Komponenten: a) eine Amidverbindung der Formel (I) A-CO-NR¹R², worin A für eine Arylgruppe oder einen aromatischen oder nicht-aromatischen, 5- oder 6-gliedrigen Heterocyclus, der 1 bis 3 Heteroatome aufweist, die ausgewählt sind unter O, N und S, steht; wobei die Arylgruppe oder der Heterocyclus gegebenenfalls 1, 2 oder 3 Substituenten aufweisen kann, die unabhängig voneinander ausgewählt sind unter Alkyl, Halogen, CHF₂, CF₃, Alkoxy, Halogenalkoxy, Alkylthio, Alkylsulfinyl und Alkylsulfonyl; R¹ für ein Wasserstoffatom steht; R² für eine Phenyl- oder Cycloalkylgruppe steht, die gegebenenfalls 1, 2 oder 3 Substituenten aufweist, die unabhängig voneinander ausgewählt sind unter Alkyl, Alkenyl, Alkynyl, Alkoxy, Alkenyloxy, Alkynyloxy, Cycloalkyl, Cycloalkenyl, Cycloalkyloxy, Cycloalkenyloxy, Phenyl und Halogen, wobei die aliphatischen und cycloaliphatischen Reste partiell oder vollständig halogeniert sein können und/oder die cycloaliphatischen Reste durch 1 bis 3 Alkylgruppen substituiert sein können und wobei die Phenylgruppe 1 bis 5 Halogenatome und/oder 1 bis 3 Substituenten aufweisen kann, die unabhängig voneinander ausgewählt sind unter Alkyl, Halogenalkyl, Alkoxy, Halogenalkoxy, Alkylthio und Halogenalkylthio, und wobei die amidische Phenylgruppe gegebenenfalls mit einem gesättigten 5-gliedrigen Ring kondensiert ist, der gegebenenfalls durch eine oder mehrere Alkylgruppen substituiert ist und/oder ein Heteroatom, ausgewählt unter O und S, aufweisen kann, und b) einen fungiziden Wirkstoff aus der Klasse der Benzimidazole oder der sie freisetzenen Vorstufen (II), in einer synergistisch wirksamen Menge.</p>			

Fungicidal mixtures based on amide compounds and benzimidazoles or precursors which release them.

5 Abstract

Fungicidal mixtures comprise as active components

a) an amide compound of the formula I

10



in which

15 A is an aryl group or an aromatic or nonaromatic, 5- or 6-membered heterocycle which has from 1 to 3 hetero atoms selected from O, N and S;

where the aryl group or the heterocycle may or may not have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, halogen, CHF_2 , 20 CF_3 , alkoxy, haloalkoxy, alkylthio, alkylsulfynyl and alkylsulfonyl;

R^1 is a hydrogen atom;

25 R^2 is a phenyl or cycloalkyl group which may or may not have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, alkenyl, alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkenyl, cycloalkyloxy, cycloalkenyloxy, phenyl and halogen, where the aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or the cycloaliphatic 30 radicals may be substituted by from 1 to 3 alkyl groups and where the phenyl group may have from 1 to 5 halogen atoms and/or from 1 to 3 substituents which are selected, independently of one another, from alkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio and haloalkylthio, and 35 where the amidic phenyl group may or may not be condensed with a saturated 5-membered ring which may or may not be substituted by one or more alkyl groups and/or may have a hetero atom selected from O and S, and

40 b) a fungicidally active ingredient from the class of the benzimidazoles or precursors which release them (II),

in a synergistically effective amount.



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Fungicidal mixtures based on amide compounds and benzimidazoles or precursors which release them.

5 The present invention relates to fungicidal mixtures for controlling harmful fungi and also to methods for controlling harmful fungi using such mixtures.

WO 97/08952 describes mixtures of amide compounds of the
10 formula I



in which

- 15 A is an aryl group or an aromatic or nonaromatic, 5- or 6-membered heterocycle which has from 1 to 3 hetero atoms selected from O, N and S;
where the aryl group or the heterocycle may or may not have 1, 2 or 3 substituents which are selected, independently of
20 one another, from alkyl, halogen, CHF_2 , CF_3 , alkoxy, haloalkoxy, alkylthio, alkylsulfynyl and alkylsulfonyl;
 R^1 is a hydrogen atom;
 R^2 is a phenyl or cycloalkyl group which may or may not have 1, 2 or 3 substituents which are selected from alkyl, alkenyl,
25 alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkenyl, cycloalkyloxy, cycloalkenyloxy, phenyl and halogen, where the aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or the cycloaliphatic radicals may be substituted by from 1 to 3 alkyl groups and
30 where the phenyl group may have from 1 to 5 halogen atoms and/or from 1 to 3 substituents which are selected, independently of one another, from alkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio and haloalkylthio, and where the amidic phenyl group may be condensed with a saturated 5-membered
35 ring which may or may not be substituted by one or more alkyl groups and/or may have a hetero atom selected from O and S, and the active ingredient fenazaquin which is known as an acaricide.

40 These mixtures are described as being particularly effective against Botrytis.

It is an object of the present invention to provide other fungicidal mixtures for controlling harmful fungi and in particular for certain indications.

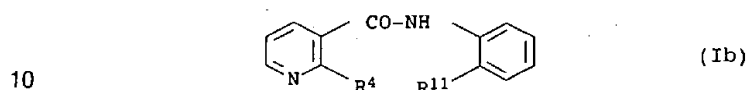
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We have found that this object is achieved by a mixture which comprises as active ingredients amide compounds of the formula Ib defined below and as a further fungicidally active component a fungicidally active ingredient from the class of the benzimidazoles or precursors which release them (II).

Accordingly, there is provided according to a first embodiment of the invention a fungicidal mixture, which comprises as active components

a) an amide compound of the formula Ib



in which

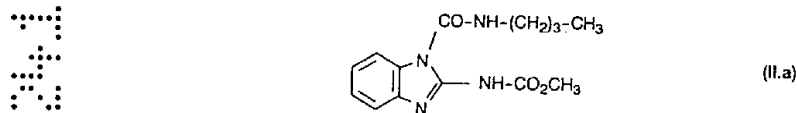
R^4 is halogen and

R^{11} is phenyl which is substituted by halogen,

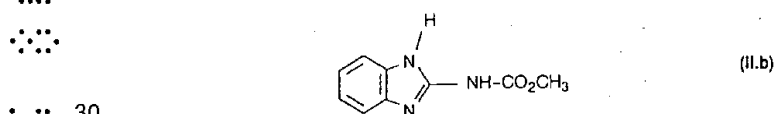
and

b) a fungicidally active compound from the class of the benzimidazoles or precursors which release them (II), selected from the group of compounds consisting of

20 II.a. methyl 1-(butylcarbamoyl) benzimidazol-2-ylcarbamate



25 II.b. methyl benzimidazol-2-ylcarbamate

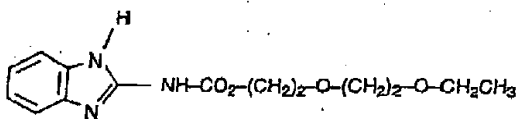


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II.c. 2-(2-ethoxyethoxy)ethyl benzimidazol-2-ylcarbamate

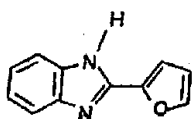
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(II.c)

II.d. 2-(2'-furyl)benzimidazole

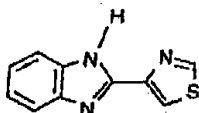
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(II.d)

II.e. 2-(1,3-thiazol-4-yl)benzimidazole

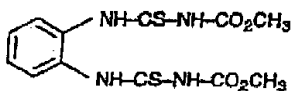
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(II.e)

20

II.f. dimethyl 4,4'-(o-phenylene)-bis-(3-thioallophanate)



(II.f)

25

in a synergistically effective amount.

As employed above and throughout this disclosure (including the claims), the following terms, unless otherwise indicated, shall be understood to have the following meanings:

30

"comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.



The mixtures according to the invention have synergistic action and are therefore particularly suitable for controlling harmful fungi and in particular powdery mildew fungi in vegetables and grapevines.

In the context of the present invention, halogen is fluorine, chlorine, 5 bromine and iodine and is in particular fluorine, chlorine and bromine.

The term "alkyl" includes straight-chain and branched alkyl groups. These are preferably straight-chain or branched C_1 - C_{12} -alkyl and in particular C_1 - C_6 -alkyl groups. Examples of alkyl groups are alkyl such as, in particular, methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, n- 10 pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethylbutyl, 2- 15 ethylbutyl, 1-ethyl-2-methylpropyl, n-heptyl, 1-methylhexyl, 1-ethylpentyl, 2-ethylpentyl, 1-propylbutyl, octyl, decyl, dodecyl.

Haloalkyl is an alkyl group as defined above which is partially or fully halogenated by one or more halogen atoms, in particular by fluorine and chlorine. Preferably, there are from 1 to 3 halogen atoms present, and the difluoromethyl or 20 trifluoromethyl group is particularly preferred.

The above statements for the alkyl group and the haloalkyl group apply in a corresponding manner to the alkyl and haloalkyl group in alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkylsulfonyl and alkylsulfonyl.

The alkenyl group includes straight-chain and branched alkenyl groups. 25 These are preferably straight-chained or branched C_3 - C_{12} -alkenyl groups and in particular C_3 - C_6 -alkenyl groups. Examples of alkenyl groups are 2-propenyl, 2-butenyl, 3-butenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 2-pentenyl, 3-pentenyl,



4-pentenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl,
 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl,
 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl,
 1,2-dimethyl-2-propenyl, 1-ethyl-2-propenyl, 2-hexenyl,
 5 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-2-pentenyl,
 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl,
 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl,
 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl,
 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl,
 10 1,1-dimethyl-3-butenyl,
 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl,
 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl,
 2,2-dimethyl-3-butenyl, 2,3-dimethyl-2-butenyl,
 2,3-dimethyl-3-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl,
 15 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl,
 1-ethyl-1-methyl-2-propenyl and 1-ethyl-2-methyl-2-propenyl, in
 particular 2-propenyl, 2-butenyl, 3-methyl-2-butenyl and
 3-methyl-2-pentenyl.

20 The alkenyl group may be partially or fully halogenated by one or more halogen atoms, in particular by fluorine or chlorine. The alkenyl group preferably has from 1 to 3 halogen atoms.

The alkynyl group includes straight-chain and branched alkynyl
 25 groups. These are preferably straight-chain and branched
 C_3-C_{12} -alkynyl groups and in particular C_3-C_6 -alkynyl groups.
 Examples of alkynyl groups are 2-propynyl, 2-butyne, 3-butyne,
 1-methyl-2-propynyl, 2-pentyne, 3-pentyne, 4-pentyne,
 1-methyl-3-butyne, 2-methyl-3-butyne, 1-methyl-2-butyne,
 30 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 2-hexynyl,
 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentyne,
 1-methyl-3-pentyne, 1-methyl-4-pentyne, 2-methyl-3-pentyne,
 2-methyl-4-pentyne, 3-methyl-4-pentyne, 4-methyl-2-pentyne,
 1,2-dimethyl-2-butyne, 1,1-dimethyl-3-butyne,
 35 1,2-dimethyl-3-butyne, 2,2-dimethyl-3-butyne,
 1-ethyl-2-butyne, 1-ethyl-3-butyne, 2-ethyl-3-butyne and
 1-ethyl-1-methyl-2-propynyl.

The above statements for the alkenyl group and its halogen
 40 substituents and for the alkynyl group apply in a corresponding
 manner to alkenyloxy and alkynyloxy.

The cycloalkyl group is preferably a C_3-C_6 -cycloalkyl group, such
 as cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. If the
 45 cycloalkyl group is substituted, it preferably has from 1 to 3
 C_1-C_4 -alkyl radicals as substituents.



Cycloalkenyl is preferably a C₄-C₆-cycloalkenyl group, such as cyclobutenyl, cyclopentenyl or cyclohexenyl. If the cycloalkenyl group is substituted, it preferably has from 1 to 3 C₁-C₄-alkyl radicals as substituents.

5

A cycloalkoxy group is preferably a C₅-C₆-cycloalkoxy group, such as cyclopentyloxy or cyclohexyloxy. If the cycloalkoxy group is substituted, it preferably has from 1 to 3 C₁-C₄-alkyl radicals as substituents.

10

The cycloalkenyloxy group is preferably a C₅-C₆-cycloalkenyloxy group, such as cyclopentyloxy or cyclohexyloxy. If the cycloalkenyloxy group is substituted, it preferably has from 1 to 3 C₁-C₄-alkyl radicals as substituents.

15

Aryl is preferably phenyl.

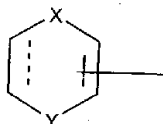
If A is a phenyl group, this may have one, two or three of the abovementioned substituents in any position. These substituents are preferably selected, independently of one another, from alkyl, difluoromethyl, trifluoromethyl and halogen, in particular chlorine, bromine and iodine. Particularly preferably, the phenyl group has a substituent in the 2-position.

25 If A is a 5-membered heterocycle, it is in particular a furyl, thiazolyl, pyrazolyl, imidazolyl, oxazolyl, thienyl, triazolyl or thiadiazolyl radical or the corresponding dihydro or tetrahydro derivatives thereof. Preference is given to a thiazolyl or pyrazolyl radical.

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If A is a 6-membered heterocycle, it is in particular a pyridyl radical or a radical of the formula:

35



40

in which one of the radicals X and Y is O, S or NR¹², where R¹² is H or alkyl, and the other of the radicals X and Y is CH₂, S, SO, SO₂ or NR⁹. The dotted line means that a double bond may or may not be present.

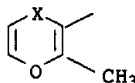


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The 6-membered aromatic heterocycle is particularly preferably a pyridyl radical, in particular a 3-pyridyl radical, or a radical of the formula

5



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(A3)

in which X is CH₂, S, SO or SO₂.

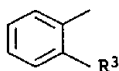
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The abovementioned heterocyclic radicals may or may not have 1, 2 or 3 of the abovementioned substituents, where these substituents are preferably selected, independently of one another, from alkyl, halogen, difluoromethyl or trifluoromethyl.

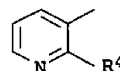
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A is particularly preferably a radical of the formulae:

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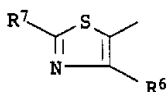


(A1)

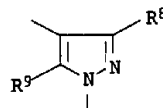


(A2)

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(A5)



(A7) CH₃

35

in which R³, R⁴, R⁶, R⁷, R⁸ and R⁹ independently of one another are hydrogen, alkyl, in particular methyl, halogen, in particular chlorine, CHF₂ or CF₃.

40

The radical R¹ in the formula I is preferably a hydrogen atom.

The radical R² in the formula I is preferably a phenyl radical. R² preferably has at least one substituent which is particularly preferably in the 2-position. The substituent (or the



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substituents) is (are) preferably selected from the group consisting of alkyl, cycloalkyl, cycloalkenyl, halogen or phenyl.

The substituents of the radical R^2 may in turn be substituted again. The aliphatic or cycloaliphatic substituents may be partially or fully halogenated, in particular fluorinated or chlorinated. They preferably have 1,2 or 3 fluorine or chlorine atoms. If the substituent of the radical R^2 is a phenyl group, this phenyl group may preferably be substituted by from 1 to 3 halogen atoms, in particular chlorine atoms, and/or by a radical which is preferably selected from alkyl and alkoxy. Particularly preferably, the phenyl group is substituted with a halogen atom in the p-position, ie the particularly preferred substituent of the radical R^2 is a p-halogen-substituted phenyl radical. The radical R^2 may also be condensed with a saturated 5-membered ring, where this ring for its part may have from 1 to 3 alkyl substituents.

R^2 is in this case, for example, indanyl, thiaindanyl and oxaindanyl. Preference is given to indanyl and 2-oxaindanyl which are attached to the nitrogen atom in particular via the 4-position.

Disclosed herein is an amide compound of the formula I in which A is as defined below:

phenyl, pyridyl, dihydropyranyl, dihydrooxathinyl, dihydrooxathiynyl oxide, dihydrooxathiynyl dioxide, furyl, thiazolyl, pyrazolyl or oxazolyl, where these groups may have 1, 2 or 3 substituents which are selected, independently of one another, from alkyl, halogen, difluoromethyl and trifluoromethyl.

It is preferred that A is one of the following groups:

pyridin-3-yl, which may or may not be substituted in the 2-position by halogen, methyl, difluoromethyl, trifluoromethyl, methoxy, methylthio, methylsulfynyl or methylsulfonyl;

phenyl which may or may not be substituted in the 2-position by methyl, trifluoromethyl, chlorine, bromine or iodine;

2-methyl-5,6-dihydropyran-3-yl;

2-methyl-5,6-dihydro-1,4-oxathiyn-3-yl or the 4-oxide or 4,4-dioxide thereof;



2-methylfuran-3-yl, which may or may not be substituted in the 4- and/or 5-position by methyl;

thiazol-5-yl, which may or may not be substituted in the 2- and/or 4-position by methyl, chlorine, difluoromethyl or trifluoromethyl;

5 thiazol-4-yl, which may or may not be substituted in the 2- and/or 5-position by methyl, chlorine, difluoromethyl or trifluoromethyl;

1-methylpyrazol-4-yl, which may or may not be substituted in the 3- and/or 5-position by methyl, chlorine, difluoromethyl or trifluoromethyl; or

10 oxazol-5-yl, which may or may not be substituted in the 2- and/or 4-position by methyl or chlorine.

There is also disclosed an amide compound of the formula I in which R^2 is a phenyl group which may or may not be substituted by 1, 2 or 3 of the abovementioned substituents.

Further disclosed is an amide compound of the formula I in which R^2 is a
15 phenyl group which has one of the following substituents in the 2-position:

C_3 - C_6 -alkyl, C_5 - C_6 -cycloalkenyl, C_5 - C_6 -cycloalkyloxy, cycloalkenyloxy, where these groups may be substituted by 1, 2 or 3 C_1 - C_4 -alkyl groups,

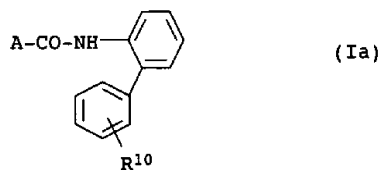
phenyl which is substituted by from 1 to 5 halogen atoms and/or from 1 to 3 groups which are selected, independently of one another, from C_1 - C_4 -alkyl, C_1 -
20 C_4 -haloalkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio and C_1 - C_4 -haloalkylthio,

indanyl or oxaindanyl which may or may not be substituted by 1, 2 or 3 C_1 - C_4 -alkyl groups.

There is still further disclosed an amide compound of the formula Ia,



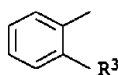
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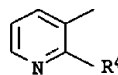
10 in which

A is

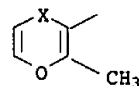
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(A1)

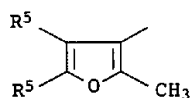


(A2)

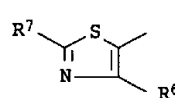


(A3)

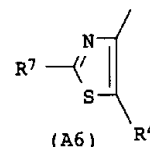
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(A4)



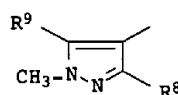
(A5)



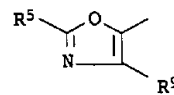
(A6)

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(A7)



(A8)

35

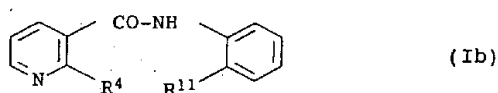
- X is methylene, sulfur, sulfinyl or sulfonyl (SO₂),
 R³ is methyl, difluoromethyl, trifluoromethyl, chlorine, bromine or iodine,
 R⁴ is trifluoromethyl or chlorine,
 40 R⁵ is hydrogen or methyl,
 R⁶ is methyl, difluoromethyl, trifluoromethyl or chlorine,
 R⁷ is hydrogen, methyl or chlorine,
 R⁸ is methyl, difluoromethyl or trifluoromethyl,
 R⁹ is hydrogen, methyl, difluoromethyl, trifluoromethyl or chlorine,
 45 R¹⁰ is C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄-alkylthio or halogen.



Lf

The amide compounds used in the fungicidal mixture of the invention are compounds of the formula Ib

5



10

in which

R^4 is halogen and

R^{11} is phenyl which is substituted by halogen.

Useful amide compounds of the formula I are mentioned in EP-A-545 099
15 and 589 301 which are incorporated herein in their entirety by reference.

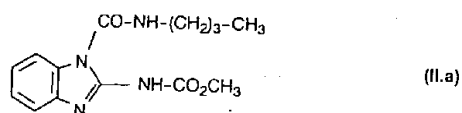
The preparation of the amide compounds of the formula I is known, for example, from EP-A-545 099 or 589 301 or can be carried out by similar processes.

The active ingredients of the formula II are the benzimidazoles or
20 precursors which release them.

Benzimidazoles or precursors which release them used in the fungicidal mixtures of the invention, are the compounds II.a to II.f below:

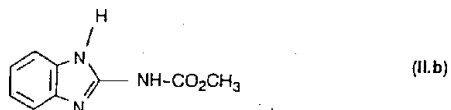
II.a: methyl 1-(butylcarbamoyl) benzimidazol-2-ylcarbamate

25



II.b: methyl benzimidazol-2-ylcarbamate

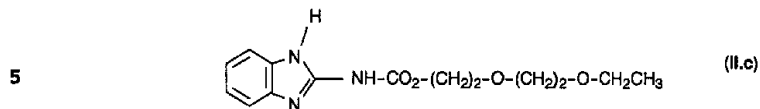
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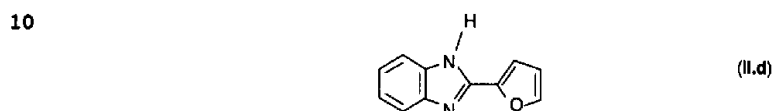
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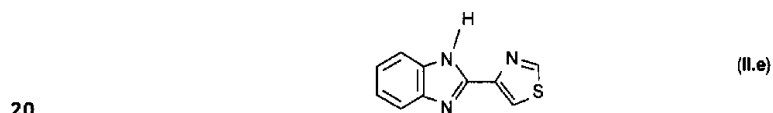
II.c: 2-(2-ethoxyethoxy)ethyl benzimidazol-2-ylcarbamate



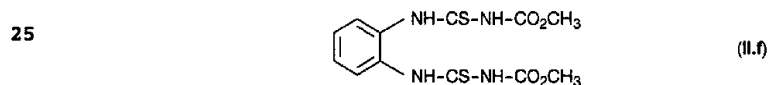
II.d: 2-(2'-furyl)benzimidazole



15 II.e: 2-(1,3-thiazol-4-yl)benzimidazole



II.f: dimethyl 4,4'-(o-phenylene)-bis(3-thioallophanate)



30 The compounds IIa to IIf are known per se:

- II.a (common name: benomyl): US-A 3,631,176, CAS RN [17804-35-2];
- II.b (common name: carbendazim): US-A 3,657,443, CAS RN [10605-21-7];
- 35 • II.c (common name: debacarb): CAS RN [62732-91-6];
- II.d (common name: fuberidazol): CAS RN [3878-19-1];
- II.e (common name: thiabendazol): US-A 3,017,415, CAS RN [148-79-8], and
- II.f (common name: thiophanat-methyl): DE-A 19 30 540, CAS RN
- 40 [23564-05-8].

To unfold synergistic activity, even a small amount of the amide compound of the formula I is sufficient. Amide compound and benzimidazole are preferably employed in a weight ratio in the
45 range of from 20:1 to 1:20, in particular from 10:1 to 1:10.



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

Examples of inorganic acids are hydrohalic acids such as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydriodic acid, sulfuric acid, phosphoric acid and nitric acid.

Suitable organic acids are, for example, formic acid, carbonic acid and alkanic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glycolic acid, thiocyanic 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), alkylphosphonic acids (phosphonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbons atoms), arylphosphonic acids or aryldiphosphonic 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, eg p-toluenesulfonic acid, salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid, 2-acetoxybenzoic acid, etc.

Suitable metal ions are, in particular, the ions of the elements of the first to eighth subgroup, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc and furthermore of the second main group, in particular calcium and magnesium, and of the third and fourth main group, in particular aluminum, tin and lead. The metals can exist, as appropriate, in the various valencies which they can assume.

When preparing the mixtures, it is preferred to employ the pure active ingredients I and II, to which further active ingredients against harmful fungi or against other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active ingredients or fertilizers can be admixed.



There is further provided according to the invention a method of controlling harmful fungi, which comprises treating the fungi, their habitat, or the materials, plants, seeds, soils, areas or spaces, to be protected against fungal attack with a fungicidal mixture of the invention where the application of the active compounds
5 amide compounds 1b and the benzimidazole or precursor which releases it may be carried out simultaneously, or in succession.

The mixtures of the compounds I and II, or the compounds I and II used simultaneously, jointly or separately, exhibit outstanding activity against a wide range of phytopathogenic fungi, in particular from the classes of the
10 Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes. Some of them act systematically



and can therefore be employed as foliar- and soil-acting fungicides.

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

10

They are particularly suitable for controlling the following phytopathogenic fungi: *Erysiphe graminis* (powdery mildew) in cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* in cucurbits, *Podosphaera leucotricha* in apples, *Uncinula necator* in 15 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 cinerea* (gray mold) in strawberries, vegetables, ornamentals and 20 grapevines, *Cercospora arachidicola* in groundnuts, *Pseudocercospora 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* 25 species in vegetables and fruit, *Mycosphaerella* species in bananas and *Fusarium* and *Verticillium* species.

The mixtures according to the invention may particularly preferably be employed for controlling powdery mildew fungi in 30 crops of grapevines and vegetables, and also in ornamentals.

The compounds I and II can be applied simultaneously, either together or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on 35 the result of the control measures.

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 0.1 to 40 5 kg/ha, in particular 0.5 to 3.0 kg/ha.

The application rates of the compounds I are from 0.01 to 2.5 kg/ha, preferably 0.05 to 2.5 kg/ha, in particular 0.1 to 1.0 kg/ha.

45



Correspondingly, in the case of the compounds II, the application rates are from 0.01 to 10 kg/ha, preferably 0.05 to 5 kg/ha, in particular 0.05 to 2.0 kg/ha.

5 For seed treatment, the application rates of the mixture are generally from 0.001 to 250 g/kg of seed, preferably 0.01 to 100 g/kg, in particular 0.01 to 50 g/kg.

If phytopathogenic harmful fungi are to be controlled, the
10 separate or joint application of the compounds I and II or of the mixtures of the compounds I and II 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.

15 The fungicidal synergistic mixtures according to the invention, or the compounds I and II, 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,
20 dusts, materials for broadcasting or granules, and applied by spraying, atomizing, dusting, broadcasting or watering. The use form depends on the intended purpose; in any case, it should ensure as fine and uniform as possible a distribution of the mixture according to the invention.

25 The formulations are prepared in a known manner, eg. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it being possible also to use other organic solvents as auxiliary solvents if water is used as
30 the diluent. Suitable auxiliaries for this purpose are essentially: solvents such as aromatics (eg. xylene), chlorinated aromatics (eg. chlorobenzenes), paraffins (eg. mineral oil fractions), alcohols (eg. methanol, butanol), ketones (eg. cyclohexanone), amines (eg. ethanolamine, dimethylformamide) and
35 water; carriers such as ground natural minerals (eg. kaolins, clays, talc, chalk) and ground synthetic minerals (eg. finely divided silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (eg. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as
40 lignosulfite waste liquors and methylcellulose.

Suitable surfactants are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, eg. ligno-, phenol-, naphthalene- and dibutyl-naphthalenesulfonic
45 acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, or fatty alcohol glycol ethers,



condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl-5 or nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, 10 lignosulfite waste liquors or methylcellulose.

Powders, materials for broadcasting and dusts can be prepared by mixing or jointly grinding the compounds I or II, or the mixture of the compounds I and II, with a solid carrier.

15

Granules (eg. coated granules, impregnated granules or homogeneous granules) are usually prepared by binding the active ingredient, or active ingredients, to a solid carrier.

20 Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicas, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials and fertilizers, such as 25 ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders or other solid carriers.

30 The formulations generally comprise from 0.1 to 95% by weight, preferably 0.5 to 90% by weight, of one of the compounds I or II or of the mixture of the compounds I and II. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR or HPLC spectra)

35

The compounds I or II, 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 40 the mixture, or of the compounds I and II in the case of separate application.

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

45

Examples of such preparations comprising the active ingredients



- I. A solution of 90 parts by weight of the active ingredients and 10 parts by weight of N-methylpyrrolidone; this solution is suitable for use in the form of microdrops;
- 5 II. A mixture of 20 parts by weight of the active ingredients, 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil; a dispersion is obtained by finely distributing the solution in water;
- 10 III. An aqueous dispersion of 20 parts by weight of the active ingredients, 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;
- 15 IV. An aqueous dispersion of 20 parts by weight of the active ingredients, 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction of boiling point 210 to 280°C, and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil;
- 20 V. A mixture, ground in a hammer mill, of 80 parts by weight of the active ingredients, 3 parts by weight of the sodium salt of diisobutyl-naphthalene-1-sulfonic acid, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel; a spray mixture is obtained by finely distributing the mixture in water;
- 25 VI. An intimate mixture of 3 parts by weight of the active ingredients and 97 parts by weight of finely divided kaolin; this dust comprises 3% by weight of active ingredient;
- 30 VII. An intimate mixture of 30 parts by weight of the active ingredients, 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel; this formulation imparts good adhesion to the active ingredient;
- 35 VIII. A stable aqueous dispersion of 40 parts by weight of the active ingredients, 10 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate, 2 parts by weight of silica gel and 48 parts by weight of water; this dispersion may be diluted further;
- 40 IX. A stable oily dispersion of 20 parts by weight of the active ingredients, 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, 8 parts by weight of fatty alcohol polyglycol ether, 20 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate
- 45



and 88 parts by weight of a paraffinic mineral oil.

Use Example

- 5 The synergistic activity of the mixtures according to the invention can be demonstrated by the following experiments:

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

Evaluation is carried out by determining the infected leaf areas in percent. These percentages are converted into efficacies. The
15 efficacy (W) is calculated as follows using Abbot's formula:

$$W = (1 - \alpha) \cdot 100 / \beta$$

- 20 α corresponds to the fungal infection of the treated plants in % and
 β corresponds to the fungal infection of the untreated (control) plants in %

- 25 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 ingredients were determined using Colby's formula [R.S. Colby, Weeds 15,
30 20-22 (1967)] and compared with the observed efficacies.

$$\text{Colby formula: } E = x + y - x \cdot y / 100$$

- 35 E expected efficacy, expressed in % of the untreated control, when using the mixture of the active ingredients A and B at the concentrations a and b
x efficacy, expressed in % of the untreated control, when using active ingredient A at the concentration a
40 y efficacy, expressed in % of the untreated control, when using active ingredient B at the concentration b

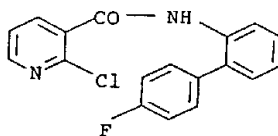
Use Example 1 - Activity against Botrytis cinerea on bell pepper leaves



Disks of green bell peppers were sprayed to runoff point with an aqueous preparation of active ingredient which had been prepared from a stock solution comprising 10% of active ingredient, 63% of cyclohexanone and 27% of emulsifier. 2 hours after the spray coating had dried on, the fruit disks were inoculated with a spore suspension of *Botrytis cinerea* containing 1.7×10^6 spores per ml of a 2% strength Biomalz solution. The inoculated fruit disks were subsequently incubated in humid chambers at 18°C for 4 days. The *Botrytis* infection on the diseased fruit disks was then evaluated visually.

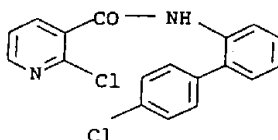
The compounds of the formula Ib used were the following components:

15



I.1

20



I.2

25

The results are shown in Tables 1 and 2 below.

30 Table 1

Ex.	Active ingredient (content in ppm)	Concentration of active ingredient in the spray liquor in ppm	Efficacy in % of the untreated control
35 1C	Control untreated	(100% infection)	0
2C	Compound I.1	4	0
3C	Compound I.2	4	40
4C	Compound II.a	4	10
40 5C	Compound II.f	4	10

45



Table 2

5	Ex.	Mixtures according to the invention (content in ppm)	Observed efficacy	Calculated efficacy*)
	6	4 ppm I.1 + 4 ppm IIa	30	10
10	7	4 ppm I.1 + 4 ppm IIb	25	10
	8	4 ppm I.2 + 4 ppm IIb	60	46

15

*) calculated using Colby's formula

The test results show that for all mixing ratios, the observed efficacy is higher than the efficacy which had been calculated beforehand using Colby's formula.

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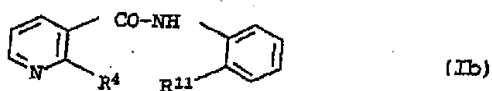
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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A fungicidal mixture, which comprises as active components

5

- a) an amide compound of the formula Ib



10

in which

R^4 is halogen and

R^{11} is phenyl which is substituted by halogen,

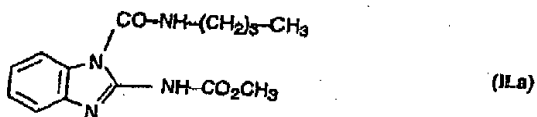
and

15

- b) a fungicidally active compound from the class of the benzimidazoles or precursors which release them (II), selected from the group of compounds consisting of

20

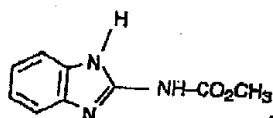
II.a: methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate



25

II.b: methyl benzimidazol-2-ylcarbamate

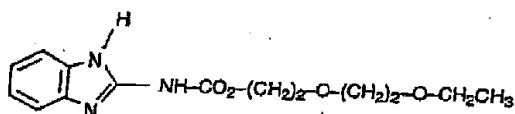




(II.b)

II.c: 2-(2-ethoxyethoxy)ethyl benzimidazol-2-ylcarbamate

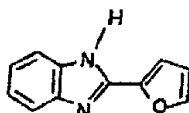
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(II.c)

II.d: 2-(2'-furyl)benzimidazole

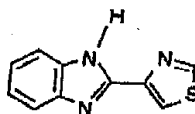
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(II.d)

II.e: 2-(1,3-thiazol-4-yl)benzimidazole

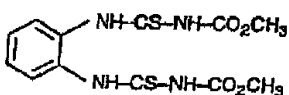
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(II.e)

II.f: dimethyl 4,4'-(o-phenylene)-bis-(3-thioallophanate)

20



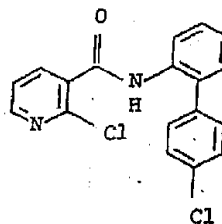
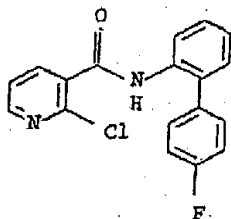
(II.f)

in a synergistically effective amount.

2. A fungicidal mixture as claimed in claim 1, which comprises as amide compound a compound of the formulae below:

25





3. A fungicidal mixture as claimed in any one of the preceding claims, which is the form of two parts, one part comprising the amide compound in a solid or liquid carrier and the other part comprising the benzimidazole or the precursor which releases it (II) in a solid or liquid carrier.
4. A fungicidal mixture, which is in the form of two parts, which mixture is substantially as herein described with reference to any one of Examples 6, 7 or 8.
5. A method of controlling harmful fungi, which comprises treating the fungi, their habitat, or the materials, plants, seeds, soils, areas or spaces to be protected against fungal attack with fungicidal mixture as claimed in any one of claims 1 to 4, where the application of the amide compounds (Ib) and the benzimidazoles or precursor which releases it (II) may be carried out simultaneously, or in succession.
6. A method according to claim 5 wherein the simultaneous application of (Ib) and (II) is together or separately.

DATED this 9th day of August 2002
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