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, alkoxyl, haloalkoxyl, 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, alkynylloxy, cy cloalkyl, cycloalkenyl, cycloalkenyl, 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, haloxy, alkylthio and haloalkylthio, and whereby the amide 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) fungicides from the group of dicarboximides, and/or c) pyrimidine derivatives of formula (II): (see formula III) in which R represents methyl, propyn-1-yl or cyclopropyl, and/or d) fludioxonil or fenpiclonil and/or captan, captafol or folpet, and/or f) fluazinam, and/or g) dichlofluanid or tollyl fluanid. The active components are provided in a synergistically effective quantity.
ABSTRACT

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, cycloalkylloxy, 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, haloxy, alkylthio 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) fungicides from the group of dicarboximides, and/or c) pyrimidine derivatives of formula (III):

![Chemical structure](image)

in which R represents methyl, propyn-1-yl or cyclopropyl, and/or d) fluoxinil or fenpiclonil and/or captan, captafol or folpet, and/or f) fluazinam, and/or g) dichlofluanid or tolyl fluanid. The active components are provided in a synergistically effective quantity.
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FUNGICIDE MIXTURES BASED ON PYRIDINE CARBOXAMIDES

This application is a division of Canadian Application No. 2,313,322 deriving from international application No. PCT/EP 98/08231 filed on December 15, 1998.

The present invention as broadly disclosed relates to fungicidal mixtures for controlling harmful fungi, which mixtures comprise amide compounds of the formula I:

\[ A-\text{CO-NR}^1\text{R}^2 \]

(I)

in which

A is an aryl group or an aromatic or non-aromatic, 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, CHF₂, CF₃, alkoxy, haloalkoxy, alkylthio, alkylsulfonyl and alkylsulfonyl;

R¹ is a hydrogen atom;

R² is a phenyl or cycloalkyl group which may or may not have 1, 2 or 3 substituents which are selected from alkyl, alkenyl, alkynyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkyl, cycloalkenyl, cycloalkyloxy, cycloalkenylloxy, 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 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 amodic 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

30 b) fungicides of the group of the dicarboximides

and/or
c) a pyrimidine derivative of the formula III,

\[
\begin{align*}
\text{III} & \quad \text{III} \\
\text{CH}_3 & \\
\text{in which } R \text{ is methyl, propyn-1-yl or cyclopropyl,} \\
\text{and/or} \\
d) \quad \text{at least one active ingredient of the formula IV or V,} \\
\text{and/or} \\
e) \quad \text{a phthalimide derivative selected from the group consisting} \\
\text{of the compounds VIa, VIb and VII} \\
\text{and/or} \\
\end{align*}
\]
and/or

f) a dinitroaniline of the formula VIII

\[ \text{VIII} \]

and/or

g) an arylsulfamide of the formula IXa or IXb

\[ \text{IXa} \]
\[ \text{IXb} \]

in a synergistically effective amount.

The present invention as claimed however is more precisely directed to a fungicidal mixture, comprising as active components

a) an amide compound of the formula (lb)

\[ \text{(lb)} \]
in which
\[ R^4 \] is halogen; and
\[ R^{11} \] is phenyl which is substituted by halogen;
and

b) a phthalimide derivative selected from the group consisting of the compounds of formulae (Vla), (Vlb) and (VII)

![Chemical structures](image)

wherein the active components are present in a synergistically effective amount.

The claimed invention also concerns a fungicidal formulation conditioned in two parts, one part comprising the amide compound of the formula (lb) as defined above in a solid or liquid carrier and the other part comprising comprising the phthalimide derivative of the formula (Vla), (Vlb) or (VII) as defined above in a solid or liquid carrier.

Moreover, the present invention provides a method for 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 formulation as previously defined, wherein the application of the two parts is carried out simultaneously or in succession.

WO 97/08952 describes fungicidal mixtures which, in addition to compounds of the formula I, also comprise fenazaquin as further components. These are described as being very effective against Botrytis.

The amide compounds of the formula I are known per se and are described in the literature (EP-A 545 099).

Fungicides from the group of the dicarboximides are known to the person skilled in the art and are commercially available.

Also known are the pyrimidine derivatives III, their preparation and their activity against harmful fungi [R=methyl: DD-A 151 404 (common name: pyrimethanil); R=1-propynyl: EP-A 224 339 (common name: mepanipyrim); R=cyclopropyl: EP-A 310 550].


US-A 2,553,770; 2,553,771; 2,553,776 describe the compounds VIa (common name: captan) and VII (common name: folpet), their preparation and their activity against harmful fungi. The compound VIIb (common name: captanol) is described in Phytopathology 52(1962), 52, 754.

Likewise, the compound VIII, its preparation and its use (CAS RN 79622-59-6, common name: fluazinam) are described in the literature.

The compounds IXa and IXb are known under the common names dichlofluanid and tolylfluanid, respectively, and are described in the German patent 1193498.

It is an object of the present inventions to provide mixtures which have an improved activity against harmful fungi combined with a reduced total amount of active ingredients applied (synergistic mixtures), with a view to reducing the application rates and to improving the activity spectrum of the known compounds.

We have found that this object is achieved by the mixtures defined at the outset. Moreover, we have found that better control of harmful fungi is possible by applying the compounds I and the compounds II to VIII simultaneously, that is either together or separately, or by applying the compounds I and the compounds II to VIII in succession than when the compounds I or II to VIII are applied on their own.

The mixtures according to the invention have synergistic action and are therefore particularly suitable for controlling harmful fungi, in particular of Botrytis species.
In the context of the present invention, halogen is fluorne, chlorine, bromine and iodine and is in particular fluorne, chlorine and bromine.

The term "alkyl" includes straight-chain and branched alkyl groups. These are preferably straight-chain or branched C₁–C₁₂-alkyl and in particular C₁–C₆-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-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 1-methylopentyl, 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-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 fluorne and chlorine. Preferably, there are from 1 to 3 halogen atoms present, and the difluoromethyl or the 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 groups in alkoxy, haloalkoxy, alkylthio, haloalkythio, alkylsulfanyl and alkylsulfonyl.

The alkenyl group includes straight-chain and branched alkenyl groups. These are preferably straight-chain or branched C₁–C₁₂-alkenyl groups and in particular C₃–C₆-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, 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, 1,1-dimethyl-3-butenyl, 1,1-dimethyl-3-butenyl,
6 1,2-dimethyl-2-buteny1, 1,2-dimethyl-3-buteny1,
1,3-dimethyl-2-buteny1, 1,3-dimethyl-3-buteny1,
2,2-dimethyl-3-buteny1, 2,3-dimethyl-2-buteny1,
2,3-dimethyl-3-buteny1, 1-ethyl-2-buteny1, 1-ethyl-3-buteny1,
2-ethyl-2-buteny1, 2-ethyl-3-buteny1, 1,1,2-trimethyl-2-propeny1,
1-ethyl-1-methyl-2-propeny1 and 1-ethyl-2-methyl-2-propeny1, in
particular 2-propeny1, 2-buteny1, 3-methyl-2-buteny1 and
3-methyl-2-penteny1.

10 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.

15 The alkynyl group includes straight-chain and branched alkynyl
groups. These are preferably straight-chain and branched
C3-C12-alkynyl groups and in particular C3-C6-alkynyl groups.
Examples of alkynyl groups are 2-propeny1, 2-buteny1, 3-buteny1,
1-methyl-2-propeny1, 2-penteny1, 3-penteny1, 4-penteny1,
1-methyl-3-buteny1, 2-methyl-3-buteny1, 1-methyl-2-buteny1,
1,1-dimethyl-2-propeny1, 1-ethyl-2-propeny1, 2-hexeny1,
3-hexeny1, 4-alkeny1 [sic], 5-hexeny1, 1-methyl-2-penteny1,
1-methyl-3-penteny1, 1-methyl-4-penteny1, 2-methyl-3-penteny1,
2-methyl-4-penteny1, 3-methyl-4-penteny1, 4-methyl-2-penteny1,
1,2-dimethyl-2-buteny1, 1,1-dimethyl-3-buteny1,
1,2-dimethyl-3-buteny1, 2,2-dimethyl-3-buteny1,
1-ethyl-2-buteny1, 1-ethyl-3-buteny1, 2-ethyl-3-buteny1 and
1-ethyl-1-methyl-2-propeny1.

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

30 The cycloalkyl group is preferably a C3-C6-cycloalkyl group, such
as cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. If the
cycloalkyl group is substituted, it preferably has from 1 to 3
C1-C4-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.
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.

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.

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.

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.

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

\[
\begin{array}{c}
\text{Y} \\
\text{X} \\
\end{array}
\]

in which one of the radicals X and Y is O, S or NR₃, where R₃ is H or alkyl, and the other of the radicals X and Y is CH₂, S, SO, SO₂ or NR₃.

The 6-membered aromatic heterocycle is particularly preferably a pyridyl radical, in particular a 3-pyridyl radical, or a radical of the formula
in which X is CH$_2$, S, SO or SO$_2$.

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.

A is particularly preferably a radical of the formulae:

in which R$^3$, R$^4$, R$^6$, R$^7$, R$^8$ and R$^9$ independently of one another are hydrogen, alkyl, in particular methyl, halogen, in particular chlorine, CHF$_2$ or CF$_3$.

The radical R$^1$ in the formula I is preferably a hydrogen atom.

The radical R$^2$ in the formula I is preferably a phenyl radical. R$^2$ preferably has at least one substituent which is particularly preferably in the 2-position. The substituent (or the substituents) is (are) preferably selected from the group consisting of alkyl, cycloalkyl, cycloalkenyl, halogen or phenyl.
The substituents of the radical R² 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 R² 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, i.e. the particularly preferred substituent of the radical R² is a p-halogen-substituted phenyl radical. The radical R² may also be condensed with a saturated 5-membered ring, where this ring for its part may have from 1 to 3 alkyl substituents.

R² 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.

According to a preferred embodiment, the composition according to the invention comprises as amide compound a compound of the formula I in which A is as defined below:

phenyl, pyridyl, dihydropyranyl, dihydrooxathiynyl, dihydrooxathiynyloxyde, 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.

According to a further preferred embodiment, 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, methylsulfinyl 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-methy1furan-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;

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

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

According to a further preferred embodiment, the compositions according to the invention comprise as amide compound a compound of the formula I in which R² is a phenyl group which may or may not be substituted by 1, 2 or 3 of the abovementioned substituents.

According to a further preferred embodiment, the compositions according to the invention comprise as amide compound a compound of the formula I in which R² is a phenyl group which has one of the following substituents in the 2-position:

C₃₋C₆-alkyl, C₅₋C₆-cycloalkenyl, C₅₋C₆-cycloalkyloxy, cycloalkenyl, where these groups may be substituted by 1, 2 or 3 C₁₋C₄-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 C₁₋C₄-alkyl, C₁₋C₄-haloalkyl, C₁₋C₄-alkoxy, C₁₋C₄-haloalkoxy, C₁₋C₄-alkythio and C₁₋C₄-haloalkythio,

indany1 or oxaindany1 which may or may not be substituted by 1, 2 or 3 C₁₋C₄-alkyl groups.

According to a further preferred embodiment, the compositions according to the invention comprise as amide compound a compound of the formula Ia,
in which

A is

(A1)  (A2)  (A3)

(A4)  (A5)  (A6)

(A7)  (A8)

X is methylene, sulfur, sulfonyl or sulfonyl (SO₂),
R³ is methyl, difluoromethyl, trifluoromethyl, chlorine, bromine
or iodine,
R⁴ is trifluoromethyl or chlorine,
R⁵ is hydrogen or methyl,
R⁶ is methyl, difluoromethyl, trifluoromethyl or chlorine,
R⁷ is hydrogen, methyl or chlorine,
R⁸ is methyl, difluoromethyl or trifluoromethyl,
R\(^9\) is hydrogen, methyl, difluoromethyl, trifluoromethyl or chlorine,
R\(^{10}\) is C\(_1\)-C\(_4\)-alkyl, C\(_1\)-C\(_4\)-alkoxy, C\(_1\)-C\(_4\)-alkylthio or halogen.

According to a particularly preferred embodiment, the compositions comprise as amide compound a compound of the formula Ib

![amide structure](image)

(Ib)

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 and 589 301.

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.

Preferred substituents R\(^{21}\) and R\(^{22}\) are hydrogen, F, Cl, methyl, ethyl, methoxy, thiomethyl and N-methylamino. R\(^3\) and R\(^4\) together may also form a grouping =O.

Preferred fungicides of the dicarboximide type are the compounds IIa to IID:

II.a: ethyl (")-3-(3,5-dichlorophenyl)-5-methyl-2,4-dioxooxazolidine-5-carboxylate

![dicarboximide structure](image)

or
II.b: 3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide

\[
\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{O} & \quad \text{CONHCH(CH}_3\text{)}_2 \\
\end{align*}
\]

or

II.c: N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide

\[
\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{O} & \quad \text{CH}_3 \\
\end{align*}
\]

or

II.d: \((RS)-3-(3,5\text{-dichlorophenyl})-5\text{-ethenyl}-5\text{-methyl-1,3-oxazolidine-2,4-dione}

\[
\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{O} & \quad \text{CH}_3 \\
\end{align*}
\]

These compounds are commercially available as fungicidally active ingredients and are described in the literature as follows:

- II.a (common name: chlozolinate): CAS RN \([84332-86-5]\), DE-A 29 06 574;
- II.c (common name: procymidone): CAS RN \([32809-16-8]\), US-A 3,903,090;

To unfold the synergistic activity, even a small amount of the amide compound of the formula I is sufficient. Preference is given to employing amide compound and active ingredient of the formula II and/or III to IX in a weight ratio in the range of from 50:1 to 1:50, in particular from 10:1 to 1:10. It is also possible here to employ ternary mixtures which, in addition to
amide compounds I, comprise both compounds II and one or more compounds III to IX. In such mixtures, the mixing ratio of the compounds II and III to IX with each other is usually in the range of from 50:1 to 1:50, preferably from 10:1 to 1:10.

Owing to the basic character of their nitrogen atoms, the compounds III, IV, V and VIII 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 alkanolic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glycolic acid, thiocyanoic 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 sulfo groups), alkylphosphonic acids (phosphonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbon atoms), arylphosphonic acids or aryldiphosphonic acids (aromatic radicals, such as phenyl and naphthyl, which carry one or two phosphoric 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 sub-group, 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 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 IX, to which further active ingredients against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active ingredients or fertilizers, can be admixed.
The mixtures of the compounds I and II and/or III to IX, or the compounds I and II and/or III to IX used simultaneously, jointly or separately, exhibit outstanding activity against a wide range of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Basidiomycetes, Phycomycetes and Deuteromycetes. Some of them act systemically 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 (e.g. 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.

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, Ucinula necator in grapevines, Puccinia species in cereals, Rhizoctonia species in cotton, rice and lawns, Ustilago species in cereals and sugar cane, Venturia inaequalis (scab) in apples, Helminthosporium species in cereals, Septoria nodorum in wheat, Botrytis cinera (gray mold) in strawberries, vegetables, ornamentals and grapevines, Cercospora arachidicola in groundnuts, Pseudocercosporella herpotrichoides in wheat and barley, Pyricularia oryzae in rice, Phytophthora infestans in potatoes and tomatoes, Plasmopara viticola in grapevines, Pseudoperonospora species in hops and cucumbers, Alternaria species in vegetables and fruit, Mycosphaerella species in bananas and Fusarium and Verticillium species.

The mixtures according to the invention may particularly preferably be employed for controlling Botrytis species in crops of grapevines and vegetables, and also in ornamentals.

The compounds I and II and/or III to IX 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 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 5 kg/ha, in particular 0.2 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.

Correspondingly, in the case of the compounds II and/or III to IX, 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.

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 separate or joint application of the compounds I and II and/or III to IX or of the mixtures of the compounds I and II and/or III to IX is effected by spraying or dusting the seeds, the plants or the soils before or after sowing of the plants, or before or after plant emergence.

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

The formulations are prepared in a known manner, 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 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 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 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 acid, and of fatty acids, alkyl- and alkylaryl sulfonates, alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, or of 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, poloxymethylene octylphenol ether, ethoxylated iso-octyl-, octyl- or nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, poloxymethylene alkyl ethers or poloxypolypropylene [sic], lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or methylcellulose.

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

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

Fillers or solid carriers are, for example, mineral earths, such as silica gel, silicas, silica gels, 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 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.

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

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

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

Examples of such preparations comprising the active ingredients are:

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;

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 to 1 mol of oleic acid N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonate, 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;

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;

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;

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 diisobutynaphthalene-1-sulfonate, 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;

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;
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;

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;

IX. A stable oily dispersion of 20 parts by weight of the active ingredients, 2 parts by weight of the calcium salt of dodecylbenzenesulfonate, 8 parts by weight of fatty alcohol polyglycol ether, 20 parts by weight of the sodium salt of a phenolsulfonic acid/urea/formaldehyde condensate and 88 parts by weight of a paraffinic mineral oil.

Use Example

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 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 efficacy ($W$) is calculated as follows using Abbot's formula:

$$ W = \left(1 - \alpha\right) \cdot \frac{100}{\beta} $$

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

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

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.
The expected efficacies of the mixtures of the active ingredients were determined using Colby's formula \([R.S. \ Colby, \ Weeds \ 15, \ 20-22 \ (1967)]\) and compared with the observed efficacies.

Colby formula: \(E = x + y - x \cdot y / 100\)

- \(E\) 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 a concentration of a
- \(y\) efficacy, expressed in % of the untreated control, when using active ingredient B at a concentration of b

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

Bell pepper seedlings of the variety "Neusiedler Ideal Elite" were, after 4-5 leaves were well developed, 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. The next day, the treated plants were inoculated with a spore suspension of Botrytis cinerea containing \(1.7 \times 10^6\) spores per ml of a 2% strength aqueous Boilerz solution. The test plants were subsequently placed in a climatized chamber with high atmospheric humidity at 22-24°C. After 5 days, the extent of the fungal infection on the leaves could be determined visually in %.

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

![Chemical structure](image-url)
The results are shown in Tables 1 and 2 below.

### Table 1

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Active ingredient</th>
<th>Concentration of active ingredient in the spray liquor in ppm</th>
<th>Efficacy in % of the untreated control</th>
</tr>
</thead>
<tbody>
<tr>
<td>1C</td>
<td>untreated</td>
<td>0 (99% infection)</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Compound I.1</td>
<td>31, 16, 8</td>
<td>78, 67, 11</td>
</tr>
<tr>
<td>15</td>
<td>Compound I.2</td>
<td>31, 16, 8</td>
<td>67, 44, 44</td>
</tr>
<tr>
<td>4C</td>
<td>Compound VIA</td>
<td>31, 16, 8</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>5C</td>
<td>Compound VII</td>
<td>31, 16, 8</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>6C</td>
<td>Compound IXa</td>
<td>31, 16, 8</td>
<td>0, 0, 0</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Mixtures according to the invention (content in ppm)</th>
<th>observed efficacy</th>
<th>calculated efficacy*</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>31 ppm I.1 + 31 ppm VIA</td>
<td>97</td>
<td>78</td>
</tr>
<tr>
<td>8</td>
<td>8 ppm I.1 + 8 ppm VIA</td>
<td>30</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td>31 ppm I.2 + 31 ppm VIA</td>
<td>100</td>
<td>67</td>
</tr>
<tr>
<td>10</td>
<td>16 ppm I.2 + 16 ppm VIA</td>
<td>70</td>
<td>44</td>
</tr>
<tr>
<td>11</td>
<td>31 ppm I.1 + 31 ppm VII</td>
<td>90</td>
<td>78</td>
</tr>
<tr>
<td>12</td>
<td>8 ppm I.1 + 8 ppm VII</td>
<td>39</td>
<td>11</td>
</tr>
<tr>
<td>Ex.</td>
<td>Mixtures according to the invention (content in ppm)</td>
<td>observed efficacy</td>
<td>calculated efficacy*</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------------------------------</td>
<td>-------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>13</td>
<td>31 ppm I.2 + 31 ppm VII</td>
<td>93</td>
<td>67</td>
</tr>
<tr>
<td>14</td>
<td>16 ppm I.2 + 16 ppm VII</td>
<td>90</td>
<td>44</td>
</tr>
<tr>
<td>15</td>
<td>8 ppm I.2 + 8 ppm VII</td>
<td>90</td>
<td>44</td>
</tr>
<tr>
<td>16</td>
<td>31 ppm I.1 + 31 ppm IXa</td>
<td>95</td>
<td>78</td>
</tr>
<tr>
<td>17</td>
<td>16 ppm I.1 + 16 ppm IXa</td>
<td>90</td>
<td>67</td>
</tr>
<tr>
<td>18</td>
<td>31 ppm I.2 + 31 ppm IXa</td>
<td>100</td>
<td>67</td>
</tr>
<tr>
<td>19</td>
<td>16 ppm I.2 + 16 ppm IXa</td>
<td>99</td>
<td>44</td>
</tr>
<tr>
<td>20</td>
<td>8 ppm I.2 + 8 ppm IXa</td>
<td>90</td>
<td>44</td>
</tr>
</tbody>
</table>

*) 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.

Use Example 2 - Activity against Botrytis cinerea on bell peppers

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 $1.7 \times 10^6$ spores per ml of a 2% strength Biomalz solution. The Botrytis infection on the diseased fruit disks was then evaluated visually.

The results are shown in Tables 3 and 4 below.
### Table 3

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Active Ingredient</th>
<th>Concentration of active ingredient in the spray liquor in ppm</th>
<th>Efficacy in % of the untreated control</th>
</tr>
</thead>
<tbody>
<tr>
<td>21C</td>
<td>untreated</td>
<td>0 (100% infection)</td>
<td>0</td>
</tr>
<tr>
<td>22C</td>
<td>Compound I.1</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>23C</td>
<td>Compound I.2</td>
<td>31</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>24C</td>
<td>Compound IV</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>25C</td>
<td>Compound VIA</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td>26C</td>
<td>Compound VII</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td>27C</td>
<td>Compound VIII</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Mixtures according to the invention (content in ppm)</th>
<th>Observed Efficacy</th>
<th>Calculated Efficacy*</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>31 ppm I.1 + 31 ppm IV</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>29</td>
<td>16 ppm I.1 + 16 ppm IV</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>31 ppm I.2 + 31 ppm IV</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>31</td>
<td>16 ppm I.2 + 16 ppm IV</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>32</td>
<td>31 ppm I.2 + 31 ppm VIA</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>33</td>
<td>31 ppm I.2 + 31 ppm VII</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>34</td>
<td>31 ppm I.1 + 31 ppm VIII</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>16 ppm I.2 + 16 ppm VIII</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>
*) 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.
WHAT IS CLAIMED IS:

1. A fungicidal mixture, comprising as active components
   
a) an amide compound of the formula (Ib)

   \[
   \begin{array}{c}
   \text{CO-NH} \\
   \text{R}^4 \quad \text{R}^{11}
   \end{array}
   \]

   in which
   
   \( R^4 \) is halogen; and
   
   \( R^{11} \) is phenyl which is substituted by halogen;

   and

   b) a phthalimide derivative selected from the group consisting of the compounds of formulae (Vla), (Vlb) and (VII)

   \[
   \begin{array}{c}
   \text{O} \\
   \text{N-SCCl}_3
   \end{array}
   \]

   (Vla)

   \[
   \begin{array}{c}
   \text{O} \\
   \text{N-SCCl}_2\text{CHCl}_2
   \end{array}
   \]

   (Vlb)

   \[
   \begin{array}{c}
   \text{O} \\
   \text{N-SCCl}_3
   \end{array}
   \]

   (VII)

   wherein the active components are present in a synergistically effective amount.
2. The fungicidal mixture as claimed in claim 1, which comprises as amide compound a compound of formula (Ib), one of the compounds of the formulae below:

![Chemical Structures]

(I.1) or (I.2).

3. A fungicidal formulation conditioned in two parts, one part comprising the amide compound of the formula (Ib) as defined in claim 1 or 2 in a solid or liquid carrier and the other part comprising a phthalimide derivative of the formula (Vla), (VIb) or (VII) as defined in claim 1 in a solid or liquid carrier.

4. A method for 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 formulation as claimed in claim 3, wherein the application of the two parts is carried out simultaneously or in succession.