



Industria y Comercio
S U P E R I N T E N D E N C I A

Organización CSA Ltda

011/067

Delegatura de Propiedad Industrial

División de Nuevas Creaciones

PCT

SOLICITUD

SUPERINTENDENCIA INDUSTRIAL Y COMERCIO
INVENTARIO

PATENTE DE INVENCION

07-134364

21. **EXPEDIENTE No.**

54. **TÍTULO** COMPOSICIONES FUNGICIDAS SINERGICAS

51. **CLASIFICACIÓN INTERNACIONAL** A01N 59/26; A01N 25/00; A01N 59/20

71. **SOLICITANTE** ISAGRO S.P.A.

DOMICILIO MILAN, ITALIA

74. **APODERADO** GERMAN CASTILLO GRAU

22. **BOGOTÁ, D. C.,** _____

PETITORIO



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-134364-00000-0000

Fecha: 2007-12-20 09:56:25 Dep. 2020 NUECREACIONI
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALII
Act. 411 PRESENTACION Folios: 114

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE

PCT

ENTRADA EN FASE NACIONAL

31 dic. 2007

1

SOLICITUD DE:

☒

Patente de Invención

☐

Patente de Modelo de Utilidad

☒

Capítulo I (Ver folio 117)

☒

Capítulo II

2

SOLICITANTE (71)

Nombre: ISAGRO S.P.A.

Dirección: Via Caldera, 21

Nacionalidad o domicilio: Milán, Italia

Lugar de Constitución: Italia

IDENTIFICACIÓN

C.C.

☐

NIT

☐

C.E.

☐

Otro

☐

Cual

Número

3

REPRESENTANTE O APODERADO

Nombre: GERMAN CASTILLO GRAU

Dirección: Carrera 13 No. 37-43 Piso 12

Teléfono: 285 74 60 Fax: 285 92 67

E-mail: info@castillograu.com

IDENTIFICACIÓN

C.C.

☒

NIT

☐

C.E.

☐

OTRO

☐

Cual

Número

17.017.671 de TP

2.978 del

Bogotá

C.S.J.

4

INVENTOR(ES) (72)

Nombre: Lucio Filippini; Marilena Gusmeroli; Silvia Mormile; Carlo Garavaglia; Luigi Mirena

Dirección: Via Morandi 13/A; Via Don Valentini, 20; Via Vicenza 9; Piazza Della Vittoria 7; Via Gamboloita, 4

Nacionalidad o Domicilio: San Donato Milanese; Monza; Novara; Cuggiono; Milán - Italia

5

PCT (86)

Solicitud Internacional No. PCT/EP/2006/005157

Fecha: Mayo 29, 2006

Publicación Internacional No. WO 2006/128677 A3

Fecha: Diciembre 7, 2006

6

Título (54) COMPOSICIONES FUNGICIDAS SINÉRGICAS

7

Clasificación Internacional (51) A01N 59/26; A01N 25/00; A01N 59/20

8

Prioridad

Si

☒

No

☐

(33) País de origen

ITALIA

(32) Fecha

Mayo 31, 2005

(31) Número de Solicitud

MI2005A001019

9

Comprobante de pago N°:

07-103 259

Fecha:

Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página.



**EXTRACTO PARA LA PUBLICACION
SOLICITUD DE PATENTE PCT
ENTRADA EN FASE NACIONAL**

.(21) No. SOLICITUD	.(51) INT.CL: A01N 59/26; A01N 25/00; A01N 59/20
.(22) FECHA DE PRESENTACION	.(71) SOLICITANTE: ISAGRO S.P.A.
.(30) PRIORIDAD	
.(31) No. DE SOLICITUD MI2005A001019	.(72) INVENTOR(ES): Lucio Filippini Marilena Gusmeroli Silvia Mormile Carlo Garavaglia Luigi Miredda
.(32) FECHA DE PRESENTACION Mayo 31, 2005	.(74) APODERADO: GERMAN CASTILLO GRAU
.(33) PAIS Italia	

.(54) TITULO: COMPOSICIONES FUNGICIDAS SINÉRGICAS

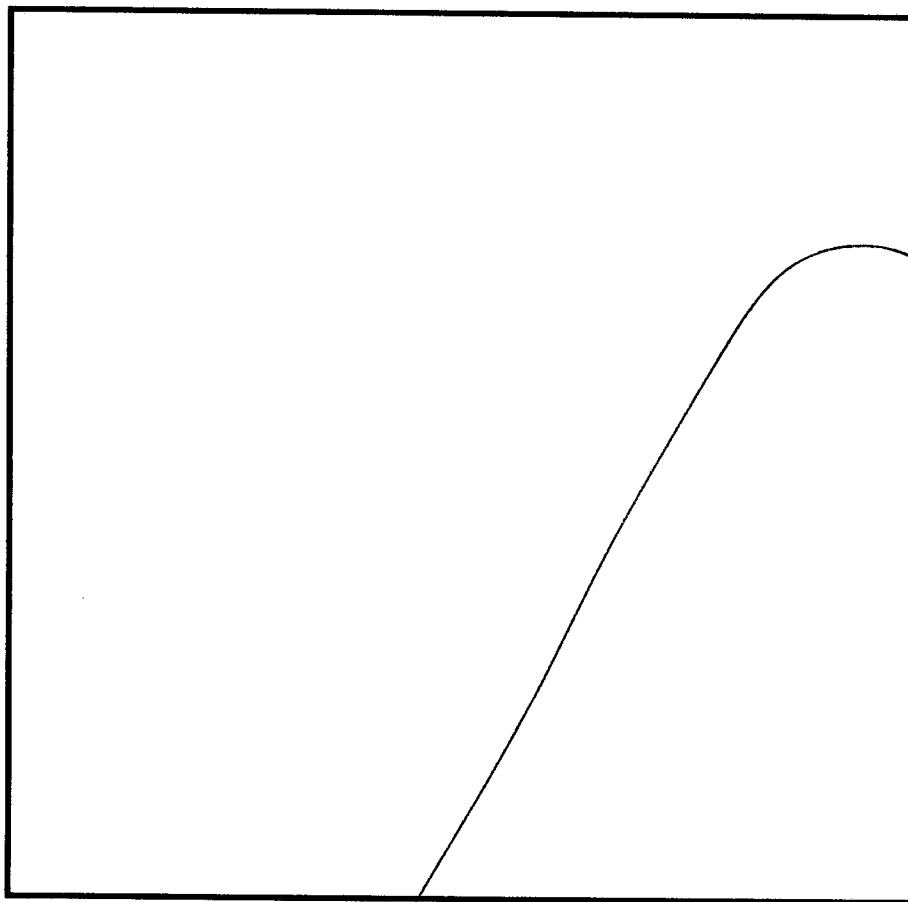
.(57) RESUMEN

composiciones que comprenden mezclas basadas en una sal cúprica (II) del ácido fosforoso, también llamada fosfito o fosfonato, con por lo menos otra sal metálica del ácido fosforoso, el uso de composiciones que comprenden mezclas basadas en una sal cúprica (II) del ácido fosforoso, también llamada fosfito o fosfonato, sola o mezclada con por lo menos otra sal metálica del ácido fosforoso, y uno o más compuestos fungicidas.

- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☒ Poderes, si fuere el caso **copia auténtica**
- ☐ Certificado de existencia y representación legal cuando el solicitante sea persona jurídica
- ☐ Documento de Cesión del inventor al solicitante o a su acusante
- ☐ Declaraciones
- ☒ Copia de la solicitud Internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos).
- ☐ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito de material biológico.
- ☐ Arte final 12 x 12
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ Otros

3

11 FIGURA CARACTERISTICA



12 Solicito la concesión de patente,

NOMBRE: GERMAN CASTILLO GRAU

FIRMA:

C.C. 17.647.671
de BogotáT.P. No. 2978
del C.S.J.

Instrucciones para la presentación de los anexos, ver reverso de esta página

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-134364-00000-0000

Fecha: 2007-12-20 09:56:25 Dep. 2020 NUECREACION
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Act. 411 PRESENTACION Folios: 114

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 07 - 103,259
FECHA : DICIEMBRE 19 DE 2007

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CASTILLO GRAU Y ASOCIADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	60633833	19/12/2007	4,607,000.00
CASTILLO GRAU Y ASOCIADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	60633835	19/12/2007	102,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		1 TRAMITES DE SOL. DE PATENTE DE IN	482,000.00
		TOTAL :	\$ 482,000.00

SON: CUATROCIENTOS OCHENTA Y DOS MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

3760 Dowling

3

Castillo Grau & Associates

Law Offices
P.O. Box 251473
Bogotá, Colombia



FOR PATENTS AND TRADEMARKS IN

COLOMBIA

PODER GENERAL

GENERAL POWER OF ATTORNEY

(1)

(1) ISAGRO S.p.A.

domiciliado en (2)

domiciled in (2)

nombra al Dr. Germán Castillo Grau y/o Adriana Castillo Gibsone y/o Luis Felipe Castillo Gibsone

Via Caldera 21 - Fabbicato D - ala 3
20153 MILANO

hereby appoint Dr. Germán Castillo Grau and/or Adriana Castillo-Gibsone and/or Luis Felipe Castillo-Gibsone

con oficinas en la Carrera 13 No. 37-43, Piso 12 en Santafé de Bogotá, D.C., Colombia como sus representantes con poder especial amplio y suficiente, para recabar de las oficinas y autoridades Colombianas, administrativas, judiciales o de policía, en primera o segunda instancia, la Obtención de Patentes de Invención, Registro de Marcas, de Diseños Industriales, de Nombres y Enseñas Comerciales, lo mismo que traspasos, extensiones, renovaciones, cambios de nombre y domicilio, registro de licencias de explotación y registro de licencias de uso referentes a tales actuaciones, a cuyo efecto les faculta para dar ante dichas autoridades todos los pasos necesarios al objeto indicado, elevar solicitudes, formular descripciones, enmiendas, protestas, declaraciones, apelaciones y reclamos, solicitar la aplicación de medidas cautelares, aceptar en nuestro nombre y representación la Cesión de derechos de invención y de patente de invención que se nos haga por cualquier persona, abonar todos los impuestos cuotas y pagos determinados por la ley, recibir todos los documentos y valores dando el descargo respectivo, llenar cualesquiera otros requisitos, desistir, y tomar en fin todas las medidas que creyeren conducentes al resguardo de nuestros intereses y en caso de presentarse oposiciones para que intervengan como demandantes o como demandados, con todas las demás facultades legales necesarias. Este poder comprende además las facultades de recibir, desistir, transigir, comprometer, sustituir, revocar sustituciones, recibir notificaciones y nombrar apoderados judiciales o extra-judiciales

with offices at Carrera 13 No. 37-43, 12th Floor in Bogotá, Colombia as our representatives with special ample and sufficient power to obtain from the offices and Colombian authorities, administrative, judicial and police, in first or in second instance, Patents of Invention, registration of Trade or Service Marks, Industrial Designs, of Commercial Names and Ensigns, as well as assignments, extensions, renewals, changes of names and addresses, registration of licences of exploitation and licences of use referring to said actions who are empowered to take before said authorities all of the necessary steps for the purposes indicated, to file applications, to formulate descriptions, corrections, protests, declarations, appeals and claims, apply for precautionary measures, to accept on our behalf and representation the assignment of rights on invention and titles of invention that may be done to us by any person, to pay all taxes, quotas and payments prescribed by law, to receive all the documents and proceeds giving the respective acquittance or receipt, to fulfill any other requisites to desist and take in fact any other measures that may be deemed conducive to the safeguard of our interests, and in case oppositions are presented to intervene as plaintiff or defendat, with all necessary legal faculties. This power includes the faculties to receive, desist, compromise, transact, substitute it in all or in part, to revoke substitutions, to receive notifications and to appoint judicial or extra-judicial attorneys.

Call

Dado y firmado en (4)

Given and signed in (4)

General Manager R&D and Commercial Operations

Firma/Signature Dr. Alessandro Mariani

Corporate Seal to be Affixed

ISAGRO S.p.A.

Como Notario Veintiséis del Circulo de Bogotá, hago constar que esta copia coincide con original que se ha presentado Bogotá D.C. - Colombia.

-7 DIC 2007

GUSTAVO SAMPER RODRIGUEZ
NOTARIO VEINTISEIS



DECLARACION NOTARIAL
(Individual)

A los días del mes de de
comparecí... personalmente ante mí, Notario
Público.....

A quien(es) doy fé de conocer y me consta que
es(son) la(s) persona(s) descrita(s) y firmante(s)
del documento que precede, declarando ante mí
que otorga(n) el mismo para los fines y
propósitos que en él se expresan.

El Notario Público

.....
(Sociedades)

El infrascrito Notario certifica: que la firma que
antecede y dice
.....

.....
es auténtica; que el signatario desempeña el
cargo de

.....
de
que tiene facultad para otorgar este poder; y que
dicha compañía está domiciliada
en.....

.....
y actualmente existe y está organizada de
acuerdo a las leyes de

.....
Todos los hechos anteriores le constan por
haber examinado los documentos respectivos y
de todo ello da fe..

Dado y firmado en.....
.....

El Notario Público

(Con Legalización Consular)

*Completado solo
por el Notario*

6

NOTARIAL CERTIFICATE
(Individuals)

On this..... day of..... of.....
personally appeared before me, a Notary Public,
.....

.....
to me known, and known to me be the person(s)
described in and who executed the foregoing
document, and he(they) duly acknowledged to
me that he(they) executed same for the uses
and purposes therein expressed.

Notary Public

.....
(Corporations)

The undersigned Notary Public certifies: that

The preceding signature reading

Alexander MARIANI

.....
is authentic; that the signor at present fills the
post of

PROXY

.....
of *ISAGRO S.A.*
and that he is empowered to grant this power;

and that said company is domiciled in.....

Milan (Italy) via Caldera 21

and actually exists and is organized in
accordance with the laws of
ITALY
all the foregoing facts are known to the Notary
due to his having examined the respective
documents to which he, the Notary, attests.

Ganted and signed
in..... this day of
January 2006

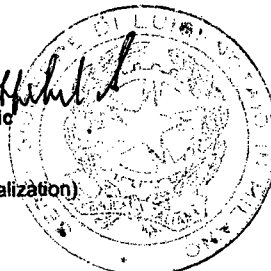
Gustavo Samper Rodriguez
Notary Public

(With Consular Legalization)

Como Notario Veintiseis del Circulo de
Bogotá, hago constar que esta copia
coincide con original que se ha presentado
Bogotá D.C. - Colombia.

-7 DIC 2007

GUSTAVO SAMPER RODRIGUEZ
NOTARIO VEINTISEIS



503 AP.

CERTIFICATO DI CONOSCERE LA LINGUA INGLESE
AI SENSI DELL'ART. 68 R.D. 1326/1914

Milano, il 19 gennaio 2006



Como Notario Veintiseis del Circulo de
Bogotá, hago constar que esta copia
coincide con original que se ha presentado
Bogotá D.C. - Colombia.

7 DIC 2007

GUSTAVO SAMPER RODRIGUEZ
NOTARIO VEINTISEIS

Convention de la Haje du 5 ottobre 1961

Paese ITALIA

Il presente atto pubblico

1. è stato sottoscritto da Giuseppe Serpi
2. agente in qualità di notaio di Milano
3. segnato dal contrassegno/timbro di

Attestato

1. a MILANO 6. il 20 GEN. 2006
2. dell'ufficio del pubblico ministero
3. sotto il numero 503 AP
4. contrassegno/timbro sigillo di notaio

AdoRizzi



Al Sost. Procuratore dell'.....
(Dott.ssa Ada Rizzi)

Como Notario Veintiseis del Circulo de
Bogotá, hago constar que esta copia
coincide con original que se ha presentado
Bogotá D.C. - Colombia.

7 DIC 2007

GUSTAVO SAMPER RODRIGUEZ
NOTARIO VEINTISEIS

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

PCT/EP2006 / 005157
International Application No.

(29.05.06) 29 MAY 2006
International Filing Date

RO/EP

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) NdP/91344

Box No. I TITLE OF INVENTION SYNERGISTIC FUNGICIDAL COMPOSITIONS	
Box No. II APPLICANT ☐ This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) ISAGRO S.p.A. Via Caldera 21 I-20153 MILANO, Italy	Telephone No. Facsimile No. Teleprinter No. Applicant's registration No. with the Office
State (that is, country) of nationality: IT	State (that is, country) of residence: IT
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) FILIPPINI Lucio Via Morandi 13/A I-20097 SAN DONATO MILANESE (Milano), Italy	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: IT	State (that is, country) of residence: IT
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) DE GREGORI Antonella COPPO Alessandro FUSINA Gerolamo ZANARDO Giovanni BARZANO' & ZANARDO MILANO S.p.A. Via Borgonuovo 10 I-20121 MILANO, Italy	Telephone No. 02 626131 Facsimile No. 02 6598859 Teleprinter No. Agent's registration No. with the Office
☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i> GUSMEROLI Marilena Via Don Valentini 20 I-20052 MONZA (Milano), Italy		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i>
Applicant's registration No. with the Office		State <i>(that is, country)</i> of nationality: IT
State <i>(that is, country)</i> of residence: IT		This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i> MORMILE Silvia Via Vicenza 9 I-28100 NOVARA, Italy		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i>
Applicant's registration No. with the Office		State <i>(that is, country)</i> of nationality: IT
State <i>(that is, country)</i> of residence: IT		This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i> GARAVAGLIA Carlo Piazza della Vittoria 7 I-20012 CUGGIONO (Milano), Italy		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i>
Applicant's registration No. with the Office		State <i>(that is, country)</i> of nationality: IT
State <i>(that is, country)</i> of residence: IT		This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i> MIRENNA Luigi Via Gamboloita 4 I-20139 MILANO, Italy		This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only <i>(If this check-box is marked, do not fill in below.)</i>
Applicant's registration No. with the Office		State <i>(that is, country)</i> of nationality: IT
State <i>(that is, country)</i> of residence: IT		This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box
☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.		

Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents. However,

- ☐ DE Germany is not designated for any kind of national protection
☐ JP Japan is not designated for any kind of national protection
☐ KR Republic of Korea is not designated for any kind of national protection
☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may only be used to exclude (irrevocably) the designations concerned if, at the time of filing, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application. See the Notes to Box No. V as to the consequences of such national law provisions in these States).

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1) (31/05/2005) 31 MAY 2005	MI2005A 001019	IT		
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)).

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EP

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

		Number of declarations
☐ Box No. VIII (i)	Declaration as to the identity of the inventor	:
☐ Box No. VIII (ii)	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	:
☐ Box No. VIII (iii)	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	:
☐ Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)	:
☐ Box No. VIII (v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	:

Box No. IX CHECK LIST; LANGUAGE OF FILING		
This international application contains: (a) on paper, the following number of sheets: request (including declaration sheets) : 4 description (excluding sequence listing and/or tables related thereto) : 45 claims : 10 abstract : 1 drawings : 1 Sub-total number of sheets : 60 sequence listing : 1 tables related thereto : 1 (for both, actual number of sheets if filed on paper, whether or not also filed in electronic form; see (c) below) Total number of sheets : 60 (b) ☐ only in electronic form (Section 801(a)(i)) (i) ☐ sequence listing (ii) ☐ tables related thereto (c) ☐ also in electronic form (Section 801(a)(ii)) (i) ☐ sequence listing (ii) ☐ tables related thereto Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the ☐ sequence listing: ☐ tables related thereto: (additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item): 1. ☒ fee calculation sheet : 1 2. ☐ original separate power of attorney : 3. ☐ original general power of attorney : 4. ☐ copy of general power of attorney; reference number, if any: 5. ☐ statement explaining lack of signature : 6. ☒ priority document(s) identified in Box No. VI as item(s): 7. ☐ translation of international application into (language): 8. ☐ separate indications concerning deposited microorganism or other biological material : 9. ☐ sequence listing in electronic form (indicate type and number of carriers) (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) : (ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter : (iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column : 10. ☐ tables in electronic form related to sequence listing (indicate type and number of carriers) (i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application) : (ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quater) : (iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column : 11. ☒ other (specify): LETTER+SUB AUTHORISATION :	Number of items
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(54) Title: SYNERGISTIC FUNGICIDAL COMPOSITIONS

(57) Abstract: Fungicidal compositions are described, consisting of mixtures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid or consisting of mixtures comprising a copper (II) salt of phosphorous acid, alone or mixed with at least another metallic salt of phosphorous acid, and one or more fungicidal compounds, and their use for the control of phytopathogen fungi.

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SYNERGISTIC FUNGICIDAL COMPOSITIONS

The present invention relates to synergistic fungicidal compositions.

10 In particular, the present invention relates to new synergistic compositions capable of controlling phytopathogens which cause considerable economic damage to agricultural crops.

More specifically, the present invention also re-
15 lates to the use of compositions comprising mixtures based on a copper (II) salt of phosphorous acid, also called phosphite or phosphonate, with at least another metallic salt of phosphorous acid and the use of compositions comprising mixtures based on a copper (II) salt of
20 phosphorous acid, also called phosphite or phosphonate, alone or mixed with at least another salt of a metal of phosphorous acid and one or more fungicidal compounds.

The use of salts of phosphorous acid as fungicides is generally known in literature, for example in American
25 patent US 4,075,324.

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The Applicant has now surprisingly found that copper (II) salts of phosphorous acid are capable of exerting a considerable synergistic effect allowing a higher fungicidal activity to be obtained, than that envisaged on the basis of the activities of single components, when applied in composition with other fungicides, in addition to providing excellent anti-resistance properties.

As resistance phenomena can arise in nature as a result of prolonged treatment with systemic fungicides, it is always important and necessary to find synergies oriented towards anti-resistance strategies.

More specifically, the Applicant has now surprisingly found that mixtures based on copper (II) salts of phosphorous acid and one or more salts of phosphorous acid obtained from metals other than copper, have a considerable synergistic effect, allowing a higher fungicidal activity to be obtained than that envisaged on the basis of the activities of single components and are capable of effectively controlling numerous diseases which can cause damage to crops of great economic interest, such as, vines, potatoes and tobacco.

Said mixtures also have an excellent toxicological and environmental profile, as well as the advantage of having a wider range of use and allowing the dosages of use of copper and also, possibly, of phosphorous acid, to

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be reduced.

Furthermore, the Applicant has surprisingly found that said mixtures of copper (II) phosphite and other metallic phosphites, in addition to copper (II) phosphite
5 alone, in turn demonstrate a significant synergy with numerous fungicidal products, having common biological targets with those of said copper (II) salt of phosphorous acid.

An object of the present invention therefore relates
10 to a fungicidal composition consisting of mixtures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid or consisting of mixtures comprising a copper (II) salt of phosphorous acid, alone or mixed with at least another
15 metallic salt of phosphorous acid, and one or more fungicidal compounds.

In particular, the metallic salt of phosphorous acid can be a salt of an alkaline, alkaline-earth metal, an ammonium salt or a salt of Fe, Mn, Zn, Ni, Al, Ti or Se.

20 Within the spirit of this invention, said mixtures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid, can be obtained either by mixing the single salts, or by coprecipitation of said salts in a reaction mixture; in
25 both cases, in the above mixture, the copper (II) salt of

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phosphorous acid and the other metallic salts of phosphorous acid can be present in any proportion, solvation state, structure and crystalline lattice composition.

The salts of an alkaline, alkaline-earth metal, ammonium salt or salts of Fe, Mn, Zn, Ni, Al, Ti or Se, of phosphorous acid can be mono- or dibasic, or they can be mixtures of these in any proportion.

In the fungicidal compositions according to the present invention, said mixtures can also contain salts of alkaline metals in percentages not higher than 10% by weight, such as reaction exchange salts which however do not have a direct fungicidal activity.

As already mentioned, an extension of said synergy concept is to obtain mixtures comprising a copper (II) salt of phosphorous acid alone or in a mixture with at least another metallic salt of phosphorous acid, and with other fungicidal compounds have common biological targets with those of said copper (II) salt of phosphorous acid.

The compound having a fungicidal activity according to the present invention is preferably selected from:

- (1) IR5885, a dipeptide compound corresponding to diastereoisomeric mixtures of methyl [S-(R,S)]-[3-(N-isopropoxycarbonylvalinyl)-amino]-3-(4-chlorophenyl)propanoate in any proportion, or to one of the two diastereoisomeric forms S-R or S-S taken

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individually;

- (2) IR6141, corresponding to N-(phenylacetyl)-N-2,6-xylyl-R- methyl alaninate;
- (3) Salicylic acid (SA) or its derivatives such as acetylsalicylic acid (ASA), copper salts of salicylic acid or acetylsalicylic acid;
- (4) A copper (I) or copper (II) salt, such as copper oxychloride, copper hydroxide, Bordeaux mixture, copper sulfate, or a mixture of copper hydroxide and oxychloride (Airone);
- (5) Benalaxyl corresponding to N-(phenylacetyl)- N-2,6-xylyl-RS-methyl alaninate;
- (6) Metalaxyl corresponding to N-(2-methoxyacetyl)-N-2,6-xylyl-RS-methyl alaninate;
- (7) Metalaxyl-M corresponding to N-(2-methoxyacetyl)-N-2,6-xylyl-R-methyl alaninate;
- (8) Oxadixyl corresponding to 2-methoxy-N-(2-oxo-1,3-oxazolidin-3-yl)aceto-2',6'-xylidide;
- (9) Ofurace corresponding to DL-3-[N-chloroacetyl-N-(2,6-xylyl)-amino]- γ -butyrolactone;
- (10) Iprovalicarb corresponding to O-(1-methyl-ethyl)-N-[2-methyl-1-[[[1-(4-methyl-phenyl)-ethyl]amino]carbonyl]propyl]carbamate;
- (11) Benthiavalicarb-isopropyl corresponding to O-isopropyl [(S)-1-{[(1R)-1-(6-fluoro-1,3-benzo-

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thiazol-2-yl)ethyl]-carbamoyl-2-methylpropyl]-
carbamate;

- (12) Cymoxanil corresponding to 1-(2-cyano-2-methoxyimino-acetyl)-3-ethylurea;
- 5 (13) Azoxystrobin corresponding to (E)-2-[2-[6-(2-cyanophenoxy)-pyrimidin-4-yloxy]phenyl-3-methylmethoxyacrylate;
- (14) Metominofen corresponding to N-methyl-(E)-methoxyimino-(2-phenoxyphenyl)acetamide;
- 10 (15) Pyraclostrobin corresponding to methyl N-(2-[1-(4-chlorophenyl)pyrazol-3-yloxymethyl]-phenyl)-N-methoxycarbamate;
- (16) Acibenzolar-S-methyl corresponding to methyl benzo(1,2,3)thiadiazole-7-thiocarboxylate;
- 15 (17) Famoxadone corresponding to 5-methyl-5-(4-phenoxyphenyl)-3-(phenylamino)oxazolidin-2,4-dione;
- (18) Fenamidone corresponding to 4-methyl-4-phenyl-1-(phenylamino)-2-methylthioimidazolidin-5-one;
- 20 (19) Cyazofamide, corresponding to 2-cyano-4-chloro-5-(4-methylphenyl)-1-(N,N dimethylaminosulfamoyl)-imidazole;
- (20) Fluazinam corresponding to 3-chloro-N-(3-chloro-5-trifluoromethyl-2-pyridyl)- α - α - α -trifluoro-2,6-
- 25 dinitro-p-toluidine;

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- (21) Dimethomorph corresponding to (E,Z)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-acryloyl]morpholine; or Flumorph (SYP-L190) corresponding to (E,Z)-4-[3-(4-fluorophenyl)-3-(3,4-dimethoxyphenyl)-acryloyl]morpholine;
- 5 (22) Flumetover corresponding to 2-(3,4-dimethoxyphenyl)-N-ethyl- α,α,α -trifluoro-N-methyl-p-toluamide;
- (23) Chlorothalonil corresponding to 1,3-dicyano-2,4,5-tetrachlorobenzene;
- 10 (24) Mancozeb corresponding to the manganese and zinc salt of ethylenebis(dithiocarbamate) (polymer);
- (25) Tolyfluanide corresponding to N-dichloro-fluoromethylthio-N',N'-dimethyl-N-p-tolylsulf-
- 15 amide;
- (26) Folpet corresponding to N-(trichloromethylthio)phthalimide;
- (27) Etridiazole corresponding to ethyl-3-trichloromethyl-1,2,4-thiadiazolyl ether;
- 20 (28) Hymexanol corresponding to 5-methylisooxazol-3-ol;
- (29) Propamocarb corresponding to propyl-(3-dimethylaminopropyl)carbamate;
- (30) R-3-aminobutanoic acid or RS-3-aminobutanoic
- 25 acid;

(31) Zoxamide, corresponding to 3,5-dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-p-toluamide;

(32) 2-(4-chlorophenyl)-N-[2-(3-methoxy-4-prop-2-inyloxy-phenyl)ethyl]-2-prop-2-inyloxy-acetamide;

5 (33) Ethaboxam, (RS)-(α-cyano-2-thienyl)-4-ethyl-2(ethylamino)-5-thiazolecarboxamide;

(34) Saccharin

The compounds (1) are described in Italian patent application Nr. MI98A002583.

10 Compound (2) is described in patent application WO 98/26654 A2.

The compounds (3) are commercial products and their copper salts are described in Italian patent application Nr. MI 2001A002430.

15 The compounds (4) are easily available on the market.

Compound (5) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 32.

20 Compound (6) is described in English patent GB 1,500,581.

Compound (7) is described in patent application WO 96/01559 A1.

25 Compound (8) is described in English patent GB 2,058,059.

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Compound (9) is described in "Phytopathological News" (1978), Vol. 9, page 142.

Compound (10) is described in patent applications EP 550,788 and EP 775,696.

5 Compound (11) is described in patent application EP 775,696.

Compound (12) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 148.

10 Compound (13) is described in European patent application EP 382,375.

Compound (14), corresponding to the experimental abbreviation SSF-126, is described in US patent 5,185,242.

15 Compound (15) is described in patent application WO 96/01258.

Compound (16) is described in US patent 4,931,581.

Compound (17) is described in "Brighton Crop Protection Conference - Pests and Diseases" 1996, Congress Records.

Compound (18) is described in European patent application EP 629,616.

Compound (19), also called IKF916, is described in
25 European patent application EP 705,823.

Compound (20) is described in European patent application EP 31,257.

The compounds (21) are described respectively in European patent application EP 219,756 and in "Brighton
5 Crop Protection Conference - Pests and Diseases" 2000, Congress Records.

Compound (22) is described in European patent applications EP 360,701 and EP 611,232.

Compound (23) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 120.
10

Compound (24) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 339.

Compound (25) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 537.
15

Compound (26) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 599.
20

Compound (27) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 252.

Compound (28) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 252.
25

cil Ed., page 314.

Compound (29) is described in "The Pesticide Manual", 1983, VIIth edition, British Crop Protection Council Ed., page 471.

5 Compound (30) is described in European patent application EP 753,258.

Compound (31) is described in "Brighton Crop Protection Conference - Pests and Diseases" 1998, Congress Records.

10 Compound (32) is described in patent application WO 01/87822.

Compound (33) is described in "The Pesticide Manual", 2003, XIIIth edition, British Crop Protection Council Ed.

15 Compound (34) is a commercial product.

Preferred fungicidal compositions according to the present invention can be selected from

- Mixture 1: CuHPO_3 + CaHPO_3 (50:50)
- Mixture 2: CuHPO_3 + ZnHPO_3 (50:50)
- 20 • Mixture 3: CuHPO_3 + MnHPO_3 (50:50)
- Mixture 4: CuHPO_3 + MnHPO_3 (66:33)
- Mixture 100: Mixture 1 + IR5885 ($750^{(1)}:15^{(2)}$)
- Mixture 103: Mixture 3 + IR5885 ($750^{(1)}:15^{(2)}$)
- Mixture 105: Mixture 2 + IR5885 ($750^{(1)}:15^{(2)}$)
- 25 • Mixture 124: CuHPO_3 + IR5885 ($750^{(1)}:15^{(2)}$)

- Mixture 125: CuHPO_3 + IR6141 ($750^{(1)}:15^{(2)}$)
- Mixture 126: Mixture 1 + IR6141 ($750^{(1)}:15^{(2)}$)
- Mixture 129: Mixture 3 + IR6141 ($750^{(1)}:15^{(2)}$)
- Mixture 131: Mixture 2 + IR6141 ($750^{(1)}:15^{(2)}$)
- 5 • Mixture 143: CuHPO_3 + $\text{Cu}(\text{SA})$ ($750^{(1)}:64^{(3)}$)
- Mixture 144: Mixture 1 + $\text{Cu}(\text{SA})$ ($750^{(1)}:64^{(3)}$)
- Mixture 145: Mixture 3 + $\text{Cu}(\text{SA})$ ($750^{(1)}:64^{(3)}$)
- Mixture 146: Mixture 2 + $\text{Cu}(\text{SA})$ ($750^{(1)}:64^{(3)}$)
- Mixture 152: CuHPO_3 + $\text{Cu}(\text{ASA})_2$ ($750^{(1)}:64^{(3)}$)
- 10 • Mixture 153: Mixture 1 + $\text{Cu}(\text{ASA})_2$ ($750^{(1)}:64^{(3)}$)
- Mixture 154: Mixture 3 + $\text{Cu}(\text{ASA})_2$ ($750^{(1)}:64^{(3)}$)
- Mixture 155: Mixture 2 + $\text{Cu}(\text{ASA})_2$ ($750^{(1)}:64^{(3)}$)
- Mixture 361: CuHPO_3 + Saccharin ($750^{(1)}:125^{(2)}$)
- Mixture 362: Mixture 1 + Saccharin ($750^{(1)}:125^{(2)}$)
- 15 • Mixture 363: Mixture 2 + Saccharin ($750^{(1)}:125^{(2)}$)
- Mixture 364: Mixture 3 + Saccharin ($750^{(1)}:125^{(2)}$)

(1): dosage expressed in ppm of equivalent phosphorous acid.

20 (2): dosage expressed in ppm of active ingredient

(3): dosage expressed in ppm of equivalent metallic copper.

The fungicidal compositions defined as mixture 1, mixture 2, mixture 3 and mixture 4 are particularly preferred.

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When they are not commercial products, the single metallic salts of phosphorous acid can be easily obtained in aqueous solution by reaction of phosphorous acid with an inorganic base such as the hydroxide or carbonate of the desired metal, or by reaction of phosphorous acid with an inorganic base, such as sodium or potassium hydroxide and the subsequent reaction with an inorganic salt, for example, chloride, bromide or sulfate of the desired metal, as described in literature in:

10 "GMelins Handbuch Der Anorganischen Chemie" Ed. Verlag Chemie - GMBH - Weinheim.

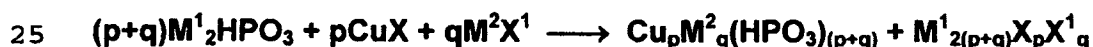
The fungicidal compositions according to the present invention can be prepared as follows: the mixtures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid are obtained by mixing the single salts or by co-precipitation of said salts in the reaction mixture.

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In this second case, the co-precipitation of the salts is effected starting from phosphites, for example sodium, potassium phosphite, by the shifting of the metallic cation M^1 with a mixture, in aqueous solution, of a copper (II) salt and the other desired metallic salt, according to scheme A:

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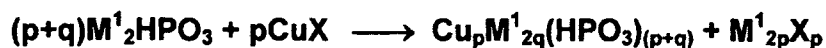
Scheme A



wherein M^1 represents a sodium or potassium atom, X represents a halogen, such as chlorine, bromine, iodine or a sulfate group, X^1 has the same meaning as X, M^2 represents an alkaline earth metal, an ammonium group or a Fe, Mn, Zn, Ni, Al, Ti, Se atom; p is a number greater than 0 and lower than 100 and q is equal to 100-p.

The co-precipitation of a copper (II) salt of phosphorous acid and a salt of an alkaline metal of phosphorous acid is effected starting from the above alkaline salt of phosphorous acid by partial shifting of the metallic cation with a suitable copper (II) salt according to scheme B:

Scheme B



wherein M^1 , X, p and q have the meanings indicated above.

Analogously mixtures comprising, in addition to copper, two or more metals selected from those listed above, can be prepared.

The fungicidal compositions according to the present invention comprising:

- a) a copper (II) salt of phosphorous mixed with at least one salt of an alkaline, alkaline earth metal, an ammonium salt or a salt of Fe, Mn, Zn, Ni, Al, Ti, Se of phosphorous acid;
- b) a copper (II) salt of phosphorous acid alone or in a

mixture with at least one salt of an alkaline, alkaline earth metal, an ammonium salt, or a salt of Fe, Mn, Zn, Ni, Al, Ti, Se of phosphorous acid, and at least one of the fungicidal compounds (1)-(34);

- 5 all have a high fungicidal activity with respect to numerous fungal species.

A further object of the present invention therefore relates to the use of a composition consisting of mixtures comprising a copper (II) salt of phosphorous acid
10 and at least another metallic salt of phosphorous acid or the use of a composition consisting of mixtures based on a copper (II) salt of phosphorous acid, alone or mixed with at least another metallic salt of phosphorous acid and one or more fungicidal compounds, in particular one
15 or more fungicidal compounds (1)-(34), for the control of phytopathogen fungi.

An object of the present invention also relates to a method for the control of phytopathogen fungi in agricultural crops by the application of a fungicidal composition
20 consisting of mixtures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid or by the application of a composition consisting of mixtures based on a copper (II) salt of phosphorous acid alone or in a mixture with at least another
25 other metallic salt of phosphorous and one or more fungi-

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cidal compounds, in particular one or more fungicidal compounds (1)-(34).

Examples of pathogens controlled by the above compositions, together with examples of the application crops, are listed hereunder for purely illustrative and non-limiting purposes:

- Plasmopara viticola (vines);
- Phytophthora infestans (tomatoes, potatoes)
- Phytophthora nicotianae (tobacco, ornamental plants);
- 10 Phytophthora palmivora (cacao);
- Phytophthora cinnamomi (pineapples, citrus fruit);
- Phytophthora capsici (peppers, tomatoes, cucurbits);
- Phytophthora cryptogea (tomatoes, plums, ornamental plants);
- 15 Phytophthora megasperma (ornamental plants);
- Phytophthora citri (citrus fruit);
- Peronospora tabacina (tabacco);
- Pseudoperonospora cubensis (cauliflowers, cucurbits);
- Pseudoperonospora umili (hops);
- 20 Phytophthora cactorum (fruit trees);
- Phytophthora destructor (onions);
- Phytophthora fragariae (strawberries) ;
- Bremia (salad).

The compositions, object of the present invention are capable of exerting a high synergistic fungicidal ac-

tivity allowing preventive, protective, prophylactic, systemic, curative and de-rooting treatment to be effected.

In the above compositions, the copper (II) salt of phosphorous acid and the other metallic salts of phosphorous acid are preferably present in a ratio varying from 10/90 to 90/10 in equivalent phosphorous acid.

Even more preferably, the copper (II) salt of phosphorous acid and the other metallic salts of phosphorous acid are present in a ratio of 50/50 in equivalent phosphorous acid.

The compositions, object of the present invention, can be used in different quantities in relation to the crop, pathogen, environmental conditions and type of formulation adopted.

The fungicidal compositions according to the present invention generally envisage the following application dosages per hectare:

- 1,000-4,000 g of salt of phosphorous acid;
- 5-3,500 g for each fungicide from (1) to (34) present in the composition.

The application of the compositions, object of the present invention, can be effected on all parts of the plant, for example on the leaves, stems, branches and roots, or on the seeds themselves before sowing, or on

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the ground in which the plant grows.

The compositions according to the present invention can be used in agronomical practice in various forms, such as for example: dry powders, wettable powders, emul-
5 sifying concentrates, micro-emulsions, pastes, granu-
lates, solutions, suspensions, etc.. The choice of the type of composition will depend on the specific use.

The compositions are prepared in the known way, for example by diluting or dissolving the active substance
10 with a solvent medium and/or a solid diluent, possibly in the presence of surface-active agents.

Solid diluents or supports which can be used are: silica, kaolin, bentonite, talc, infusorial earth, dolomite, calcium carbonate, magnesia, gypsum, clays, syn-
15 thetic silicates, attapulgite, sepiolite.

Liquid diluents which can be used, are for example, in addition to water, aromatic compounds (xylols or blends of alkylbenzols), paraffins (petroleum fractions), alcohols (methanol, propanol, butanol, octanol, glycer-
20 ine), amines, amides (N,N-dimethylformamide, N-methylpyrrolidone), ketones (cyclohexanone, acetone, acetophenone, isophorone, ethylamylketone), fatty acids (for example, vegetable oils such as rape oil, sunflower oil), esters (isobutyl acetate, methyl esters of fatty acids
25 obtained for example from the transesterification of

vegetable oils).

Sodium salts, calcium salts, triethanolamine or triethylamine of alkylsulfonates, alkylaryl sulphonates, polyethoxylated alkylphenols, fatty alcohols condensed
5 with ethylene oxide, polyethoxylated fatty acids, polyethoxylated esters of sorbitol, ligninsulphonates, can be used as surface-active agents.

The compositions can also contain special additives for particular purposes, such as for example, adhesive
10 agents, such as gum Arabic, polyvinyl alcohol, polyvinyl pyrrolidone.

In the fungicidal compositions, object of the present invention, the concentration of active substances varies from 0.1% to 98% by weight, preferably from 0.5%
15 to 90% by weight.

When desired, other compatible active principles can be added to the compositions, object of the present invention, such as, for example, phyto-regulators, antibiotics, herbicides, insecticides, fertilizers.

20 The following examples are provided for purely illustrative and non-limiting purposes of the present invention.

Example 1:

Preparation of the copper and calcium salt of phosphorous
25 acid (50:50). Mixture 1.

350 g of H_3PO_3 and 350 ml of H_2O are charged into a 6 l flask. 563.5 g of KOH dissolved in 700 ml of H_2O and previously cooled to about 30°C are added dropwise under stirring on an ice bath. After a few minutes, the aqueous solution obtained by dissolution of 364 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 313.95 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in 3500 ml of H_2O is added dropwise. The blue-green precipitate which is formed is left under stirring for 24 hours at room temperature, the flask is then heated bringing the internal temperature to about 80°C and the mixture is left under stirring for a further 4 hours approximately. The hot mixture is filtered on a Buchner funnel and the solid is washed with 3500 ml of H_2O previously heated to about 80°C . After drying in an oven, 652 g of the desired product are obtained.

Elemental analysis [% found (theoretical)]=

Cu 20.9 (21.2); Ca 13.0 (13.4); P 20.5 (20.7).

Example 2:

Preparation of the copper and zinc salt of phosphorous acid (50:50). Mixture 2.

350 g of H_3PO_3 and 350 ml of H_2O are charged into a 6 l flask. 563.5 g of KOH dissolved in 700 ml of H_2O and previously cooled to about 30°C are added dropwise under stirring on an ice bath. After a few minutes, the aqueous solution obtained by dissolution of 364 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

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and 613.9 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 3500 ml of H_2O is added dropwise. The blue precipitate which is formed is left under stirring for 24 hours at room temperature, the flask is then heated bringing the internal temperature to about 80°C and the mixture is left under stirring for a further 4 hours approximately. The hot mixture is filtered on a Buchner funnel and the solid is washed with 3500 ml of H_2O previously heated to about 80°C. After drying in an oven, 699 g of the desired product are obtained.

10 Elemental analysis [% found (theoretical)]=

Cu 18.6 (21.2); Zn 16.6 (13.4); P 18.4 (20.7); K 4.18 (0).

Example 3:

Preparation of the copper and manganese salt of phosphorous acid (50:50). Mixture 3.

350 g of H_3PO_3 and 350 ml of H_2O are charged into a 6 l flask. 563.5 g of KOH dissolved in 700 ml of H_2O and previously cooled to about 30°C are added dropwise under stirring on an ice bath. After a few minutes, the aqueous solution obtained by dissolution of 364 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 360.86 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 3500 ml of H_2O is added dropwise. The blue precipitate which is formed is left under stirring for 24 hours at room temperature, the flask is then heated bringing the internal temperature to about 80°C and the mixture is left under stirring for a further

4 hours approximately. The hot mixture is filtered on a Buchner funnel and the solid is washed with 3500 ml of H₂O previously heated to about 80°C. After drying in an oven, 451.7 g of the desired product are obtained.

5 Elemental analysis [% found (theoretical)]=

Cu 20.3 (21.4); Mn 16.8 (18.5); P 20.0 (20.9); K 1.49 (0).

Example 4:

Preparation of the copper and manganese salt of phospho-
10 rous acid (66:33). Mixture 4.

350 g of H₃PO₃ and 350 ml of H₂O are charged into a 6 l flask. 563.5 g of KOH dissolved in 700 ml of H₂O and previously cooled to about 30°C are added dropwise under stirring on an ice bath. After a few minutes, the aqueous
15 solution obtained by dissolution of 480.4 g of CuCl₂*2H₂O and 238.2 g of MnSO₄*H₂O in 3500 ml of H₂O is added dropwise. The blue precipitate which is formed is left under stirring for 24 hours at room temperature, the flask is then heated bringing the internal temperature to about
20 80°C and the mixture is left under stirring for a further 4 hours approximately. The hot mixture is filtered on a Buchner funnel and the solid is washed with 3500 ml of H₂O previously heated to about 80°C. After drying in an oven, 482 g of the desired product are obtained.

25 Elemental analysis [% found (theoretical)]=

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Cu 27.7 (28.2); Mn 10.9 (12.2); P 18.0 (20.9); K 0.97 (0).

The following mixtures can be obtained with an analogous procedure:

- 5 • Mixture 5: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (34:66) *
- Mixture 6: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (66:34) *
- Mixture 7: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (25:75) *
- Mixture 8: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (75:25) *
- Mixture 9: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (90:10) *
- 10 • Mixture 10: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (10:90) *
- Mixture 11: $\text{CuHPO}_3 + \text{CaHPO}_3$ (34:66) *
- Mixture 12: $\text{CuHPO}_3 + \text{CaHPO}_3$ (66:34) *
- Mixture 13: $\text{CuHPO}_3 + \text{CaHPO}_3$ (25:75) *
- Mixture 14: $\text{CuHPO}_3 + \text{CaHPO}_3$ (75:25) *
- 15 • Mixture 15: $\text{CuHPO}_3 + \text{CaHPO}_3$ (90:10) *
- Mixture 16: $\text{CuHPO}_3 + \text{CaHPO}_3$ (10:90) *
- Mixture 17: $\text{CuHPO}_3 + \text{MnHPO}_3$ (34:66) *
- Mixture 18: $\text{CuHPO}_3 + \text{MnHPO}_3$ (25:75) *
- Mixture 19: $\text{CuHPO}_3 + \text{MnHPO}_3$ (75:25) *
- 20 • Mixture 20: $\text{CuHPO}_3 + \text{MnHPO}_3$ (90:10) *
- Mixture 21: $\text{CuHPO}_3 + \text{MnHPO}_3$ (10:90) *
- Mixture 22: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (50:50) *
- Mixture 23: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (34:66) *
- Mixture 24: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (66:34) *
- 25 • Mixture 25: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (25:75) *

- Mixture 26: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (75:25) *
- Mixture 27: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (90:10) *
- Mixture 28: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (10:90) *
- Mixture 29: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (50:50) *
- 5 • Mixture 30: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (34:66) *
- Mixture 31: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (66:34) *
- Mixture 32: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (25:75) *
- Mixture 33: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (75:25) *
- Mixture 34: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (90:10) *
- 10 • Mixture 35: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (10:90) *
- Mixture 36: $\text{CuHPO}_3 + \text{NiHPO}_3$ (50:50) *
- Mixture 37: $\text{CuHPO}_3 + \text{NiHPO}_3$ (34:66) *
- Mixture 38: $\text{CuHPO}_3 + \text{NiHPO}_3$ (66:34) *
- Mixture 39: $\text{CuHPO}_3 + \text{NiHPO}_3$ (25:75) *
- 15 • Mixture 40: $\text{CuHPO}_3 + \text{NiHPO}_3$ (75:25) *
- Mixture 41: $\text{CuHPO}_3 + \text{NiHPO}_3$ (90:10) *
- Mixture 42: $\text{CuHPO}_3 + \text{NiHPO}_3$ (10:90) *
- Mixture 43: $\text{CuHPO}_3 + \text{MgHPO}_3$ (50:50) *
- Mixture 44: $\text{CuHPO}_3 + \text{MgHPO}_3$ (34:66) *
- 20 • Mixture 45: $\text{CuHPO}_3 + \text{MgHPO}_3$ (66:34) *
- Mixture 46: $\text{CuHPO}_3 + \text{MgHPO}_3$ (25:75) *
- Mixture 47: $\text{CuHPO}_3 + \text{MgHPO}_3$ (75:25) *
- Mixture 48: $\text{CuHPO}_3 + \text{MgHPO}_3$ (90:10) *
- Mixture 49: $\text{CuHPO}_3 + \text{MgHPO}_3$ (10:90) *
- 25 • Mixture 50: $\text{CuHPO}_3 + \text{BaHPO}_3$ (50:50) *

- Mixture 51: CuHPO_3 + BaHPO_3 (34:66) *
- Mixture 52: CuHPO_3 + BaHPO_3 (66:34) *
- Mixture 53: CuHPO_3 + BaHPO_3 (25:75) *
- Mixture 54: CuHPO_3 + BaHPO_3 (75:25) *
- 5 • Mixture 55: CuHPO_3 + BaHPO_3 (90:10) *
- Mixture 56: CuHPO_3 + BaHPO_3 (10:90) *
- Mixture 57: CuHPO_3 + K_2HPO_3 (50:50) *
- Mixture 58: CuHPO_3 + K_2HPO_3 (34:66) *
- Mixture 59: CuHPO_3 + K_2HPO_3 (66:34) *
- 10 • Mixture 60: CuHPO_3 + K_2HPO_3 (25:75) *
- Mixture 61: CuHPO_3 + K_2HPO_3 (75:25) *
- Mixture 62: CuHPO_3 + K_2HPO_3 (90:10) *
- Mixture 63: CuHPO_3 + K_2HPO_3 (10:90) *
- Mixture 64: CuHPO_3 + $(\text{NH}_4)_2\text{HPO}_3$ (50:50) *
- 15 • Mixture 65: CuHPO_3 + $(\text{NH}_4)_2\text{HPO}_3$ (34:66) *
- Mixture 66: CuHPO_3 + $(\text{NH}_4)_2\text{HPO}_3$ (66:34) *
- Mixture 67: CuHPO_3 + $(\text{NH}_4)_2\text{HPO}_3$ (25:75) *
- Mixture 68: CuHPO_3 + $(\text{NH}_4)_2\text{HPO}_3$ (75:25) *
- Mixture 69: CuHPO_3 + $(\text{NH}_4)_2\text{HPO}_3$ (90:10) *
- 20 • Mixture 70: CuHPO_3 + $(\text{NH}_4)_2\text{HPO}_3$ (10:90) *
- Mixture 71: CuHPO_3 + $\text{Ti}(\text{HPO}_3)_2$ (50:50) *
- Mixture 72: CuHPO_3 + $\text{Ti}(\text{HPO}_3)_2$ (34:66) *
- Mixture 73: CuHPO_3 + $\text{Ti}(\text{HPO}_3)_2$ (66:34) *
- Mixture 74: CuHPO_3 + $\text{Ti}(\text{HPO}_3)_2$ (25:75) *
- 25 • Mixture 75: CuHPO_3 + $\text{Ti}(\text{HPO}_3)_2$ (75:25) *

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- Mixture 76: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (90:10) *
- Mixture 77: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (10:90) *
- Mixture 78: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (50:50) *
- Mixture 79: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (34:66) *
- 5 • Mixture 80: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (66:34) *
- Mixture 81: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (25:75) *
- Mixture 82: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (75:25) *
- Mixture 83: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (90:10) *
- Mixture 84: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (10:90) *
- 10 • Mixture 85: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{MnHPO}_3$ (34:33:33) *
- Mixture 86: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{MnHPO}_3$ (50:25:25) *
- Mixture 87: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{ZnHPO}_3$ (34:33:33) *
- Mixture 88: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{ZnHPO}_3$ (50:25:25) *
- Mixture 89: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{MnHPO}_3$ (34:33:33) *
- 15 • Mixture 90: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{MnHPO}_3$ (50:25:25) *
- Mixture 91: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{K}_2\text{HPO}_3$ (34:33:33) *
- Mixture 92: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{K}_2\text{HPO}_3$ (50:25:25) *
- Mixture 93: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{K}_2\text{HPO}_3$ (25:25:50) *
- Mixture 94: $\text{CuHPO}_3 + \text{MnHPO}_3 + \text{K}_2\text{HPO}_3$ (34:33:33) *
- 20 • Mixture 95: $\text{CuHPO}_3 + \text{MnHPO}_3 + \text{K}_2\text{HPO}_3$ (50:25:25) *
- Mixture 96: $\text{CuHPO}_3 + \text{MnHPO}_3 + \text{K}_2\text{HPO}_3$ (25:25:50) *
- Mixture 97: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{K}_2\text{HPO}_3$ (34:33:33) *
- Mixture 98: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{K}_2\text{HPO}_3$ (50:25:25) *
- Mixture 99: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{K}_2\text{HPO}_3$ (25:25:50) *
- 25 • Mixture 100: Mixture 1 + IR5885 (750⁽¹⁾:15⁽²⁾)

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- Mixture 101: Mixture 57 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 102: Mixture 91 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 103: Mixture 3 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 104: Mixture 94 + IR5885 (750⁽¹⁾:15⁽²⁾)
- 5 • Mixture 105: Mixture 2 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 106: Mixture 97 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 107: Mixture 29 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 108: CuHPO₃+Fe₂(HPO₃)₃+K₂HPO₃ (34:33:33) *
- Mixture 109: Mixture 108 + IR5885 (750⁽¹⁾:15⁽²⁾)
- 10 • Mixture 110: Mixture 22 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 111: CuHPO₃+Al₂(HPO₃)₃+K₂HPO₃ (34:33:33) *
- Mixture 112: Mixture 111 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 113: Mixture 64 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 114: CuHPO₃+(NH₄)₂HPO₃+CaHPO₃ (34:33:33) *
- 15 • Mixture 115: Mixture 114 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 116: CuHPO₃ +(NH₄)₂HPO₃ +ZnHPO₃ (34:33:33) *
- Mixture 117: Mixture 116 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 118: CuHPO₃ +(NH₄)₂HPO₃+MnHPO₃ (34:33:33) *
- Mixture 119: Mixture 118 + IR5885 (750⁽¹⁾:15⁽²⁾)
- 20 • Mixture 120: CuHPO₃ +(NH₄)₂HPO₃ + Fe₂(HPO₃)₃ (34:33:33) *
- Mixture 121: Mixture 120+ IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 122: CuHPO₃ + (NH₄)₂HPO₃ + Al₂(HPO₃)₃ (34:33:33) *
- Mixture 123: Mixture 122 + IR5885 (750⁽¹⁾:15⁽²⁾)
- Mixture 124: CuHPO₃ + IR5885 (750⁽¹⁾:15⁽²⁾)
- 25 • Mixture 125: CuHPO₃ + IR6141 (750⁽¹⁾:15⁽²⁾)

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- Mixture 126: Mixture 1 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 127: Mixture 57 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 128: Mixture 91 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 129: Mixture 3 + IR6141 (750⁽¹⁾:15⁽²⁾)
- 5 • Mixture 130: Mixture 94 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 131: Mixture 2 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 132: Mixture 97 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 133: Mixture 29 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 134: Mixture 108 + IR6141 (750⁽¹⁾:15⁽²⁾)
- 10 • Mixture 135: Mixture 22 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 136: Mixture 111 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 137: Mixture 64 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 138: Mixture 114 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 139: Mixture 116 + IR6141 (750⁽¹⁾:15⁽²⁾)
- 15 • Mixture 140: Mixture 118 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 141: Mixture 120 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 142: Mixture 122 + IR6141 (750⁽¹⁾:15⁽²⁾)
- Mixture 143: CuHPO₃ + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- Mixture 144: Mixture 1 + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- 20 • Mixture 145: Mixture 3 + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- Mixture 146: Mixture 2 + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- Mixture 147: Mixture 22 + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- Mixture 148: Mixture 57 + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- Mixture 149: Mixture 64 + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- 25 • Mixture 150: Mixture 91 + Cu(SA) (750⁽¹⁾:64⁽³⁾)

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- Mixture 151: Mixture 114 + Cu(SA) (750⁽¹⁾:64⁽³⁾)
- Mixture 152: CuHPO₃ + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- Mixture 153: Mixture 1 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- Mixture 154: Mixture 3 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- 5 • Mixture 155: Mixture 2 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- Mixture 156: Mixture 22 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- Mixture 157: Mixture 57 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- Mixture 158: Mixture 64 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- Mixture 159: Mixture 91 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- 10 • Mixture 160: Mixture 114 + Cu(ASA)₂ (750⁽¹⁾:64⁽³⁾)
- Mixture 161: CuHPO₃ + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 162: Mixture 1 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 163: Mixture 2 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 164: Mixture 3 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- 15 • Mixture 165: Mixture 22 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 166: Mixture 57 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 167: Mixture 64 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 168: Mixture 91 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 169: Mixture 114 + Benalaxyl (750⁽¹⁾:15⁽²⁾)
- 20 • Mixture 170: CuHPO₃ + Metalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 171: Mixture 1 + Metalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 172: Mixture 2 + Metalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 173: Mixture 3 + Metalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 174: Mixture 22 + Metalaxyl (750⁽¹⁾:15⁽²⁾)
- 25 • Mixture 175: Mixture 57 + Metalaxyl (750⁽¹⁾:15⁽²⁾)

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- Mixture 176: Mixture 64 + Metalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 177: Mixture 91 + Metalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 178: Mixture 114 +Metalaxyl (750⁽¹⁾:15⁽²⁾)
- Mixture 179: CuHPO₃ + Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- 5 • Mixture 180: Mixture 1+ Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- Mixture 181: Mixture 2+ Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- Mixture 182: Mixture 3+ Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- Mixture 183:Mixture 22+ Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- Mixture 184:Mixture 57+ Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- 10 • Mixture 185:Mixture 64+ Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- Mixture 186:Mixture 91+ Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- Mixture 187:Mixture 114+Metalaxyl-M (750⁽¹⁾:15⁽²⁾)
- Mixture 188: CuHPO₃ + Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- Mixture 189: Mixture 1+ Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- 15 • Mixture 190: Mixture 2+ Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- Mixture 191: Mixture 3+ Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- Mixture 192 Mixture 22+ Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- Mixture 193:Mixture 57+ Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- Mixture 194:Mixture 64+ Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- 20 • Mixture 195:Mixture 91+ Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- Mixture 196:Mixture 114+Iprovalicarb(750⁽¹⁾:15⁽²⁾)
- Mixture 197: CuHPO₃ + Axoxystrobin (750⁽¹⁾:10⁽²⁾)
- Mixture 198: Mixture 1 +Axoxystrobin(750⁽¹⁾:10⁽²⁾)
- Mixture 199: Mixture 2 +Axoxystrobin(750⁽¹⁾:10⁽²⁾)
- 25 • Mixture 200: Mixture 3 +Axoxystrobin(750⁽¹⁾:10⁽²⁾)

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- Mixture 201: Mixture 22+Axoxystrobin(750⁽¹⁾:10⁽²⁾)
- Mixture 202: Mixture 57+Axoxystrobin(750⁽¹⁾:10⁽²⁾)
- Mixture 203: Mixture 64+Axoxystrobin(750⁽¹⁾:10⁽²⁾)
- Mixture 204: Mixture 91+Axoxystrobin(750⁽¹⁾:10⁽²⁾)
- 5 • Mixture 205:Mixture 114+Axoxystrobin(750⁽¹⁾:10⁽²⁾)
- Mixture 206: CuHPO₃ + Metominofen(750⁽¹⁾:10⁽²⁾)
- Mixture 207: Mixture 1+ Metominofen(750⁽¹⁾:10⁽²⁾)
- Mixture 208:Mixture 2 + Metominofen(750⁽¹⁾:10⁽²⁾)
- Mixture 209:Mixture 3 + Metominofen(750⁽¹⁾:10⁽²⁾)
- 10 • Mixture 210:Mixture 22 + Metominofen(750⁽¹⁾:10⁽²⁾)
- Mixture 211:Mixture 57 + Metominofen(750⁽¹⁾:10⁽²⁾)
- Mixture 212:Mixture 64 + Metominofen(750⁽¹⁾:10⁽²⁾)
- Mixture 213:Mixture 91 + Metominofen(750⁽¹⁾:10⁽²⁾)
- Mixture 214:Mixture 114+ Metominofen(750⁽¹⁾:10⁽²⁾)
- 15 • Mixture 215:CuHPO₃ + Acibenzolar (750⁽¹⁾:20⁽²⁾)
- Mixture 216:Mixture 1 + Acibenzolar(750⁽¹⁾:20⁽²⁾)
- Mixture 217:Mixture 2 + Acibenzolar(750⁽¹⁾:20⁽²⁾)
- Mixture 218:Mixture 3 + Acibenzolar(750⁽¹⁾:20⁽²⁾)
- Mixture 219:Mixture 22 + Acibenzolar(750⁽¹⁾:20⁽²⁾)
- 20 • Mixture 220:Mixture 57 + Acibenzolar(750⁽¹⁾:20⁽²⁾)
- Mixture 221:Mixture 64 + Acibenzolar(750⁽¹⁾:20⁽²⁾)
- Mixture 222:Mixture 91 + Acibenzolar(750⁽¹⁾:20⁽²⁾)
- Mixture 223:Mixture 114+ Acibenzolar(750⁽¹⁾:20⁽²⁾)
- Mixture 224:CuHPO₃ + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- 25 • Mixture 225:Mixture 1 + Cyazofamide(750⁽¹⁾:10⁽²⁾)

HB

- Mixture 226: Mixture 2 + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- Mixture 227: Mixture 3 + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- Mixture 228: Mixture 22 + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- Mixture 229: Mixture 57 + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- 5 • Mixture 230: Mixture 64 + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- Mixture 231: Mixture 91 + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- Mixture 232: Mixture 114 + Cyazofamide (750⁽¹⁾:10⁽²⁾)
- Mixture 233: CuHPO₃ + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- Mixture 234: Mixture 1 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- 10 • Mixture 235: Mixture 2 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- Mixture 236: Mixture 3 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- Mixture 237: Mixture 22 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- Mixture 238: Mixture 57 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- Mixture 239: Mixture 64 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- 15 • Mixture 240: Mixture 91 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- Mixture 241: Mixture 114 + Chlorothalonil (750⁽¹⁾:100⁽²⁾)
- Mixture 242: CuHPO₃ + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- Mixture 243: Mixture 1 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- Mixture 244: Mixture 2 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- 20 • Mixture 245: Mixture 3 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- Mixture 246: Mixture 22 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- Mixture 247: Mixture 57 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- Mixture 248: Mixture 64 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- Mixture 249: Mixture 91 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)
- 25 • Mixture 250: Mixture 114 + Bordeaux mixt. (750⁽¹⁾:200⁽³⁾)

HH

- Mixture 251: $\text{CuHPO}_3 + \text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- Mixture 252: Mixture 1 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- Mixture 253: Mixture 2 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- Mixture 254: Mixture 3 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- 5 • Mixture 255: Mixture 22 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- Mixture 256: Mixture 57 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- Mixture 257: Mixture 64 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- Mixture 258: Mixture 91 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- Mixture 259: Mixture 114 + $\text{Cu}(\text{OH})_2$ (750⁽¹⁾:100⁽³⁾)
- 10 • Mixture 260: $\text{CuHPO}_3 + \text{CuSO}_4$ (750⁽¹⁾:100⁽³⁾)
- Mixture 261: Mixture 1 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- Mixture 262: Mixture 2 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- Mixture 263: Mixture 3 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- Mixture 264: Mixture 22 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- 15 • Mixture 265: Mixture 57 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- Mixture 266: Mixture 64 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- Mixture 267: Mixture 91 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- Mixture 268: Mixture 114 + CuSO_4 (750⁽¹⁾:100⁽³⁾)
- Mixture 269: $\text{CuHPO}_3 + \text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (750⁽¹⁾:200⁽³⁾)
- 20 • Mixture 270: Mixture 1 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (750⁽¹⁾:200⁽³⁾)
- Mixture 271: Mixture 2 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (750⁽¹⁾:200⁽³⁾)
- Mixture 272: Mixture 3 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (750⁽¹⁾:200⁽³⁾)
- Mixture 273: Mixture 22 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (750⁽¹⁾:200⁽³⁾)
- Mixture 274: Mixture 57 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (750⁽¹⁾:200⁽³⁾)
- 25 • Mixture 275: Mixture 64 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (750⁽¹⁾:200⁽³⁾)

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- Mixture 276: Mixture 91 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}:200^{(3)}$)
- Mixture 277: Mixture 114 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}:200^{(3)}$)
- Mixture 278: CuHPO_3 + Airone ($750^{(1)}:40^{(3)}$)
- Mixture 279: Mixture 1 + Airone ($750^{(1)}:40^{(3)}$)
- 5 • Mixture 280: Mixture 2 + Airone ($750^{(1)}:40^{(3)}$)
- Mixture 281: Mixture 3 + Airone ($750^{(1)}:40^{(3)}$)
- Mixture 282: Mixture 22 + Airone ($750^{(1)}:40^{(3)}$)
- Mixture 283: Mixture 57 + Airone ($750^{(1)}:40^{(3)}$)
- Mixture 284: Mixture 64 + Airone ($750^{(1)}:40^{(3)}$)
- 10 • Mixture 285: Mixture 91 + Airone ($750^{(1)}:40^{(3)}$)
- Mixture 286: Mixture 114 + Airone ($750^{(1)}:40^{(3)}$)
- Mixture 287: CuHPO_3 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- Mixture 288: Mixture 1 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- Mixture 289: Mixture 2 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- 15 • Mixture 290: Mixture 3 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- Mixture 291: Mixture 22 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- Mixture 292: Mixture 57 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- Mixture 293: Mixture 64 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- Mixture 294: Mixture 91 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- 20 • Mixture 295: Mixture 114 + Pyraclostrobin ($750^{(1)}:10^{(2)}$)
- Mixture 296: CuHPO_3 + Benthiavalicarb ($750^{(1)}:15^{(2)}$)
- Mixture 297: Mixture 1 + Benthiavalicarb ($750^{(1)}:15^{(2)}$)
- Mixture 298: Mixture 2 + Benthiavalicarb ($750^{(1)}:15^{(2)}$)
- Mixture 299: Mixture 3 + Benthiavalicarb ($750^{(1)}:15^{(2)}$)
- 25 • Mixture 300: Mixture 22 + Benthiavalicarb ($750^{(1)}:15^{(2)}$)

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- Mixture 301: Mixture 57 + Benthiavalicarb (750⁽¹⁾:15⁽²⁾)
- Mixture 302: Mixture 64 + Benthiavalicarb (750⁽¹⁾:15⁽²⁾)
- Mixture 303: Mixture 91 + Benthiavalicarb (750⁽¹⁾:15⁽²⁾)
- Mixture 304: Mixture 114 + Benthiavalicarb (750⁽¹⁾:15⁽²⁾)
- 5 • Mixture 305: CuHPO₃ + Cymoxanil (750⁽¹⁾:100⁽²⁾)
- Mixture 306: Mixture 1 + Cymoxanil (750⁽¹⁾:100⁽²⁾)
- Mixture 307: Mixture 2 + Cymoxanil (750⁽¹⁾:100⁽²⁾)
- Mixture 308: Mixture 3 + Cymoxanil (750⁽¹⁾:100⁽²⁾)
- Mixture 309: CuHPO₃ + Oxadixyl (750⁽¹⁾:15⁽²⁾)
- 10 • Mixture 310: Mixture 1 + Oxadixyl (750⁽¹⁾:15⁽²⁾)
- Mixture 311: Mixture 2 + Oxadixyl (750⁽¹⁾:15⁽²⁾)
- Mixture 312: Mixture 3 + Oxadixyl (750⁽¹⁾:15⁽²⁾)
- Mixture 313: CuHPO₃ + Ofurace (750⁽¹⁾:15⁽²⁾)
- Mixture 314: Mixture 1 + Ofurace (750⁽¹⁾:15⁽²⁾)
- 15 • Mixture 315: Mixture 2 + Ofurace (750⁽¹⁾:15⁽²⁾)
- Mixture 316: Mixture 3 + Ofurace (750⁽¹⁾:15⁽²⁾)
- Mixture 317: CuHPO₃ + Famoxadone (750⁽¹⁾:100⁽²⁾)
- Mixture 318: Mixture 1 + Famoxadone (750⁽¹⁾:100⁽²⁾)
- Mixture 319: Mixture 2 + Famoxadone (750⁽¹⁾:100⁽²⁾)
- 20 • Mixture 320: Mixture 3 + Famoxadone (750⁽¹⁾:100⁽²⁾)
- Mixture 321: CuHPO₃ + Fenamidone (750⁽¹⁾:50⁽²⁾)
- Mixture 322: Mixture 1 + Fenamidone (750⁽¹⁾:50⁽²⁾)
- Mixture 323: Mixture 2 + Fenamidone (750⁽¹⁾:50⁽²⁾)
- Mixture 324: Mixture 3 + Fenamidone (750⁽¹⁾:50⁽²⁾)
- 25 • Mixture 325: CuHPO₃ + Fluazinam (750⁽¹⁾:100⁽²⁾)

HA

- Mixture 326: Mixture 1 + Fluazinam (750⁽¹⁾:100⁽²⁾)
- Mixture 327: Mixture 2 + Fluazinam (750⁽¹⁾:100⁽²⁾)
- Mixture 328: Mixture 3 + Fluazinam (750⁽¹⁾:100⁽²⁾)
- Mixture 329: CuHPO₃ + Dimethomorph (750⁽¹⁾:100⁽²⁾)
- 5 • Mixture 330: Mixture 1 + Dimethomorph (750⁽¹⁾:100⁽²⁾)
- Mixture 331: Mixture 2 + Dimethomorph (750⁽¹⁾:100⁽²⁾)
- Mixture 332: Mixture 3 + Dimethomorph (750⁽¹⁾:100⁽²⁾)
- Mixture 333: CuHPO₃ + Mancozeb (750⁽¹⁾:200⁽²⁾)
- Mixture 334: Mixture 1 + Mancozeb (750⁽¹⁾:200⁽²⁾)
- 10 • Mixture 335: Mixture 2 + Mancozeb (750⁽¹⁾:200⁽²⁾)
- Mixture 336: Mixture 3 + Mancozeb (750⁽¹⁾:200⁽²⁾)
- Mixture 337: CuHPO₃ + Tolyfluanide (750⁽¹⁾:100⁽²⁾)
- Mixture 338: Mixture 1 + Tolyfluanide (750⁽¹⁾:100⁽²⁾)
- Mixture 339: Mixture 2 + Tolyfluanide (750⁽¹⁾:100⁽²⁾)
- 15 • Mixture 340: Mixture 3 + Tolyfluanide (750⁽¹⁾:100⁽²⁾)
- Mixture 341: CuHPO₃ + Folpet (750⁽¹⁾:100⁽²⁾)
- Mixture 342: Mixture 1 + Folpet (750⁽¹⁾:100⁽²⁾)
- Mixture 343: Mixture 2 + Folpet (750⁽¹⁾:100⁽²⁾)
- Mixture 344: Mixture 3 + Folpet (750⁽¹⁾:100⁽²⁾)
- 20 • Mixture 345: CuHPO₃ + Propamocarb (750⁽¹⁾:200⁽²⁾)
- Mixture 346: Mixture 1 + Propamocarb (750⁽¹⁾:200⁽²⁾)
- Mixture 347: Mixture 2 + Propamocarb (750⁽¹⁾:200⁽²⁾)
- Mixture 348: Mixture 3 + Propamocarb (750⁽¹⁾:200⁽²⁾)
- Mixture 349: CuHPO₃ + Zoxamide (750⁽¹⁾:100⁽²⁾)
- 25 • Mixture 350: Mixture 1 + Zoxamide (750⁽¹⁾:100⁽²⁾)

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- Mixture 351: Mixture 2 + Zoxamide (750⁽¹⁾:100⁽²⁾)
- Mixture 352: Mixture 3 + Zoxamide (750⁽¹⁾:100⁽²⁾)
- Mixture 353: CuHPO₃ + Syngenta⁽⁴⁾ (750⁽¹⁾:15⁽²⁾)
- Mixture 354: Mixture 1 + Syngenta⁽⁴⁾ (750⁽¹⁾:15⁽²⁾)
- 5 • Mixture 355: Mixture 2 + Syngenta⁽⁴⁾ (750⁽¹⁾:15⁽²⁾)
- Mixture 356: Mixture 3 + Syngenta⁽⁴⁾ (750⁽¹⁾:15⁽²⁾)
- Mixture 357: CuHPO₃ + Ethaboxam (750⁽¹⁾:50⁽²⁾)
- Mixture 358: Mixture 1 + Ethaboxam (750⁽¹⁾:50⁽²⁾)
- Mixture 359: Mixture 2 + Ethaboxam (750⁽¹⁾:50⁽²⁾)
- 10 • Mixture 360: Mixture 3 + Ethaboxam (750⁽¹⁾:50⁽²⁾)
- Mixture 361: CuHPO₃ + Saccharin (750⁽¹⁾:125⁽²⁾)
- Mixture 362: Mixture 1 + Saccharin (750⁽¹⁾:125⁽²⁾)
- Mixture 363: Mixture 2 + Saccharin (750⁽¹⁾:125⁽²⁾)
- Mixture 364: Mixture 3 + Saccharin (750⁽¹⁾:125⁽²⁾)
- 15 *: reciprocal proportions expressed in equivalent phosphorous acid.

(1): dose expressed in ppm of equivalent phosphorous acid.

(2): dose expressed in ppm of active ingredient.

20 (3): dose expressed in ppm of equivalent metal copper.

(4): fungicidal compound (32).

Example 5

Efficacy of the fungicidal compositions, object of the present invention, in the control of Plasmopara viticola
25 on vines in preventive leaf application.

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Tables 1-2

Leaves of cultivar Merlot vines, grown in vases, in a conditioned environment ($20 \pm 1^\circ\text{C}$, 70% relative humidity) are treated by spraying both sides of the leaves with the mixtures under examination dispersed in an aqueous solution containing a 0.3% of tween 20.

After remaining 7 days in a conditioned environment, the plants are infected on the lower side with an aqueous suspension of spores of *Plasmopara viticola* (200,000 spores per cm^3).

The plants are kept in a humidity saturated environment, at 21°C , for the incubation period of the fungus and, at the end of this period (7 days), the fungicidal activity is evaluated according to an evaluation percentage scale from 100 (healthy plant) to 0 (completely infected plant).

From the data indicated in tables 1-2, it is possible to verify the synergistic effect of the mixtures, consisting of the mixtures being examined, compared with the expected efficacy using the Limpel formula ("Pesticide Science" (1987), vol. 19, pages 309-315):

$$E = x + y - (xy/100)$$

wherein:

- E is the fungicidal activity expected, in the absence of synergistic effects, from a mixture obtained

b0

by mixing $g.\underline{x}$ of compound X with $g.\underline{y}$ of compound Y;

- x is the activity of compound X when used alone
with a dosage of $g.\underline{x}$;

- y is the activity of compound Y when used alone
5 with a dosage of $g.\underline{y}$.

When the fungicidal activity found experimentally is
greater than the value of E , this activity is considered
synergistic.

Table 1

10 7-day preventive activity on *Plasmopara viticola*, with
leaf application on vines, of mixtures (50:50)* of copper
(II) salt of phosphorous acid ($CuHPO_3$), which at 500
ppm** ($g.\underline{x}$) is 88 (x) with other metallic salts of phos-
phorous acid.

15

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Mixture	Dose ppm** ($g.\underline{y}$)	Activity (y)	Activity Mixture according to Limpel (E)	Experimental activity of mixture	Synergy factor
$CaHPO_3$	500	0	88	100	1.14
$ZnHPO_3$	500	25	91	100	1.10
$MnHPO_3$	500	0	88	98	1.11
$(NH_4)_2HPO_3$	500	38	92.5	98	1.06
K_2HPO_3	500	45	93.4	99	1.06

* reciprocal proportions expressed in equivalent phospho-
25 rous acid.

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** the doses in ppm refer to the quantity of equivalent phosphorous acid.

Table 2

7-day preventive activity on *Plasmopara viticola*, with
5 leaf application on vines, of mixtures of the Saccharin
compound (compound Nr. 34), which at 500 ppm (g.x) is 45
(x) with one or more metallic salts of phosphorous acid.

10	Mixture	Dose ppm** (g.y)	Activity (y)	Activity Mixture according to Limpel (E)	Experimental activity of mixture	Synergy factor
	CuHPO ₃	250	35	64.2	100	1.56
	CuHPO ₃ + CaHPO ₃ (50:50)*	250	50	72.5	100	1.38
15	CuHPO ₃ + ZnHPO ₃ (50:50)*	250	52	73.6	98	1.33
	CuHPO ₃ + MnHPO ₃ (50:50)*	250	47	70.8	95	1.34
20	CuHPO ₃ + MnHPO ₃ (66:34)*	250	56	75.8	98	1.29

* reciprocal proportions expressed in equivalent phosphorous acid.

** the doses in ppm refer to the quantity of equivalent phosphorous acid.

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Example 6

Efficacy of the fungicidal compositions, object of the present invention, in the control of Phytophthora infestans on potato plants in preventive leaf application.

5 **Tables 3-6**

Leaves of potato plants, of the Primura variety, grown in vases, in a conditioned environment ($20 \pm 1^\circ\text{C}$, 70% relative humidity) are treated by spraying both sides of the leaves with the mixtures under examination dispersed
10 in an aqueous solution containing 0.3% of tween 20.

After remaining 7 days in a conditioned environment, the plants are infected on the lower side with an aqueous suspension of spores of *Phytophthora infestans* (100,000 spores per cm^3).

15 The plants are kept in a humidity saturated environment, at $18-24^\circ\text{C}$, for the incubation period of the fungus and, at the end of this period (7 days), the fungicidal activity is evaluated according to an evaluation percentage scale from 100 (healthy plant) to 0 (completely in-
20 fected plant).

From the data indicated in tables 3-6, it is possible to verify the synergic effect of the mixtures, consisting of the mixtures being examined, compared with the expected efficacy using the Limpel formula.

Table 3

7-day preventive activity on *Phytophthora infestans*, with leaf application on potato plants, of mixtures (50:50)* of copper (II) salt of phosphorous acid (CuHPO_3), which at 750 ppm** (g.x) is 12 (x) with other metallic salts of phosphorous acid.

Mixture	Dose ppm** (g.y)	Activity (y)	Activity Mixture according to Limpel (E)	Experimental activity of mixture	Synergy factor
CaHPO_3	750	10	18.8	78	4.1
ZnHPO_3	750	5	16.4	70	4.2
MnHPO_3	750	15	25.2	80	3.2
$(\text{NH}_4)_2\text{HPO}_3$	750	5	16.4	68	4.1
K_2HPO_3	750	5	16.4	65	3.9

* reciprocal proportions expressed in equivalent phosphorous acid.

** the doses in ppm refer to the quantity of equivalent phosphorous acid.

Table 4

7-day preventive activity on *Phytophthora infestans*, with leaf application on potato plants, of mixtures of the compound IR5885 (compound Nr. 1), which at 15 ppm (g.x) is 40 (x) with one or more metallic salts of phosphorous acid.

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5	Mixture	Dose ppm** (g.y)	Activity (y)	Activity Mixture according to Limpel (E)	Experimental activity of mixture	Synergy factor
	CuHPO ₃	750	12	47.2	95	2.01
10	CuHPO ₃ + CaHPO ₃ (50:50) *	750	78	86.8	95	1.09
	CuHPO ₃ + ZnHPO ₃ (50:50) *	750	70	82	90	1.1
	CuHPO ₃ + MnHPO ₃ (50:50) *	750	80	88	93	1.05
15	CuHPO ₃ + MnHPO ₃ (66:34) *	750	75	78.7	90	1.14

* reciprocal proportions expressed in equivalent phosphorous acid.

** the doses in ppm refer to the quantity of equivalent
20 phosphorous acid.

Table 5

7-day preventive activity on *Phytophthora infestans*, with
leaf application on potato plants, of mixtures of the
compound IR6141(compound Nr. 2), which at 50 ppm (g.x) is
25 35 (x) with one or more metallic salts of phosphorous

acid.

5	Mixture	Dose ppm** (g.y)	Activity (y)	Activity Mixture according to Limpel (E)	Experimental activity of mixture	Synergy factor
	CuHPO ₃	750	12	42.8	90	2.10
10	CuHPO ₃ + CaHPO ₃ (50:50) *	750	78	85.7	94	1.09
	CuHPO ₃ + ZnHPO ₃ (50:50) *	750	70	80.5	93	1.15
	CuHPO ₃ + MnHPO ₃ (50:50) *	750	80	87	96	1.10
15	CuHPO ₃ + MnHPO ₃ (66:34) *	750	77	85	94	1.1

* reciprocal proportions expressed in equivalent phosphorous acid.

20 ** the doses in ppm refer to the quantity of equivalent phosphorous acid.

Table 6

7-day preventive activity on *Phytophthora infestans*, strain resistant to phenylalanine, with leaf application
25 on potato plants, of mixtures of the compound

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IR6141 (compound Nr. 2), which at 50 ppm (g.x) is 5 (x) with one or more metallic salts of phosphorous acid.

5		Mixture	Dose ppm** (g.y)	Activity (y)	Activity Mixture according to Limpel (E)	Experimental activity of mixture	Synergy factor
		CuHPO ₃	750	12	16.4	85	5.2
10		CuHPO ₃ + CaHPO ₃ (50:50) *	750	78	79.1	90	1.14
		CuHPO ₃ + ZnHPO ₃ (50:50) *	750	70	71.5	88	1.23
		CuHPO ₃ + MnHPO ₃ (50:50) *	750	80	81	94	1.16
15		CuHPO ₃ + MnHPO ₃ (66:34) *	750	77	78.1	90	1.15

* reciprocal proportions expressed in equivalent phosphorous acid.

20 ** the doses in ppm refer to the quantity of equivalent phosphorous acid.

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CLAIMS

- 5 1. A fungicidal composition consisting of mixtures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid or consisting of mixtures comprising a copper (II) salt of phosphorous acid, alone or mixed with at
10 least another metallic salt of phosphorous acid, and one or more fungicidal compounds.
2. The fungicidal composition according to claim 1, characterized in that the metallic salt of phosphorous acid is a salt of an alkaline, alkaline earth
15 metal, an ammonium salt or a salt of Fe, Mn, Zn, Ni, Al, Ti or Se.
3. The fungicidal composition according to claim 1, characterized in that the metallic salt of phosphorous acid is a mono- or di-basic salt, or a mixture
20 of these in any proportion.
4. The fungicidal composition according to claim 1, characterized in that the mixtures also contain alkaline metals in percentages not higher than 10% by weight.
- 25 5. The fungicidal composition according to claim 1,

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characterized in that the fungicidal compound is selected from:

- (1) IR5885, a dipeptide compound corresponding to diastereoisomeric mixtures of methyl [S-(R,S)]-[3-(N-isopropoxycarbonylvalinyl)-amino]-3-(4-chloro-phenyl)propanoate in any proportion, or to one of the two diastereoisomeric forms S-R or S-S taken individually;
- (2) IR6141, corresponding to N-(phenylacetyl)-N-2,6-xylyl-R- methyl alaninate;
- (3) Salicylic acid (SA) or its derivatives such as acetylsalicylic acid (ASA), copper salts of salicylic acid or acetylsalicylic acid;
- (4) A copper (I) or copper (II) salt, such as copper oxychloride, copper hydroxide, Bordeaux mixture, copper sulfate, or a mixture of copper hydroxide and oxychloride (Airone);
- (5) Benalaxyl corresponding to N-(phenylacetyl) -N-2,6-xylyl-RS-methyl alaninate;
- (6) Metalaxyl corresponding to N-(2-methoxyacetyl)-N-2,6-xylyl-RS-methyl alaninate;
- (7) Metalaxyl-M corresponding to N-(2-methoxyacetyl)-N-2,6-xylyl-R-methyl alaninate;
- (8) Oxadixyl corresponding to 2-methoxy-N-(2-oxo-1,3-oxazolidin-3-yl)aceto-2',6'-xylidide;

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- (9) Ofurace corresponding to DL-3-[N-chloroacetyl-N-(2,6-xylyl)-amino]- γ -butyrolactone;
- (10) Iprovalicarb corresponding to O-(1-methyl-ethyl)-N-[2-methyl-1-[[[1-(4-methyl-phenyl)-ethyl]amino]carbonyl]propyl]carbamate;
- (11) Benthiavalicarb-isopropyl corresponding to O-isopropyl [(S)-1-{[(1R)-1-(6-fluoro-1,3-benzothiazol-2-yl)ethyl]-carbamoyl-2-methylpropyl}-carbamate;
- (12) Cymoxanil corresponding to 1-(2-cyano-2-methoxyimino-acetyl)-3-ethylurea;
- (13) Azoxystrobin corresponding to (E)-2-[2-[6-(2-cyanophenoxy)-pyrimidin-4-yloxy]phenyl-3-methylmethoxyacrylate;
- (14) Metominofen corresponding to N-methyl-(E)-methoxyimino-(2-phenoxyphenyl)acetamide;
- (15) Pyraclostrobin corresponding to methyl N-(2-[1-(4-chlorophenyl)pyrazol-3-yloxymethyl]-phenyl)-N-methoxycarbamate;
- (16) Acibenzolar-S-methyl corresponding to methyl benzo(1,2,3)thiadiazole-7-thiocarboxylate;
- (17) Famoxadone corresponding to 5-methyl-5-(4-phenoxyphenyl)-3-(phenylamino)oxazolidin-2,4-dione;
- (18) Fenamidone corresponding to 4-methyl-4-phenyl-1-

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- (phenylamino)-2-methylthioimidazolidin-5-one;
- (19) Cyazofamide, corresponding to 2-cyano-4-chloro-5-(4-methylphenyl)-1-(N,N-dimethylamino-sulfamoyl)imidazole;
- 5 (20) Fluazinam corresponding to 3-chloro-N-(3-chloro-5-trifluoromethyl-2-pyridyl)- α - α - α -trifluoro-2,6-dinitro-p-toluidine;
- (21) Dimethomorph corresponding to (E,Z)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-
- 10 acryloyl]morpholine; or Flumorph (SYP-L190) corresponding to (E,Z)-4-[3-(4-fluorophenyl)-3-(3,4-dimethoxyphenyl)-acryloyl]morpholine;
- (22) Flumetover corresponding to 2-(3,4-dimethoxyphenyl)-N-ethyl- α , α , α -trifluoro-N-methyl-
- 15 p-toluamide;
- (23) Chlorothalonil corresponding to 1,3-dicyano-2,4,5,6-tetrachlorobenzene;
- (24) Mancozeb corresponding to the manganese and zinc salt of ethylenebis(dithiocarbamate) (polymer);
- 20 (25) Tolyfluanide corresponding to N-dichloro-fluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide;
- (26) Folpet corresponding to N-(trichloromethylthio)phthalimide;
- 25 (27) Etridiazole corresponding to ethyl-3-

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trichloromethyl-1,2,4-thiadiazolyl ether;

(28) Hymexanol corresponding to 5-methyliso-oxazol-3-ol;

5 (29) Propamocarb corresponding to propyl-(3-dimethylaminopropyl)carbamate;

(30) R-3-aminobutanoic acid or RS-3-aminobutanoic acid;

(31) Zoxamide, corresponding to 3,5-dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-p-toluamide;

10 (32) 2-(4-chlorophenyl)-N-[2-(3-methoxy-4-prop-2-inyloxy-phenyl)ethyl]-2-prop-2-inyloxy-acetamide;

(33) Ethaboxam, (RS)-(α-cyano-2-thienyl)-4-ethyl-2(ethylamino)-5-thiazolecarboxamide;

(34) Saccharin

15 6. The fungicidal composition according to claim 1, characterized in that the copper (II) salt of phosphorous acid and the other metallic salts of phosphorous acid are present in a ratio ranging from 10/90 to 90/10 in equivalent phosphorous acid.

20 7. The fungicidal composition according to claim 1, characterized in that the copper (II) salt of phosphorous acid and the other metallic salts of phosphorous acid are present in a 50/50 ratio in equivalent phosphorous acid.

25 8. The fungicidal composition according to claim 1,

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characterized in that the concentration of active substances, the copper (II) salt of phosphorous acid, the other metallic salts of phosphorous acid and/or the fungicidal compounds, ranges from 0.1% to 98% by weight, preferably from 0.5% to 90% by weight.

9. The fungicidal composition according to claim 1, characterized in that it consists of a mixture selected from:

- 10 • Mixture 1: CuHPO_3 + CaHPO_3 (50:50)
- Mixture 2: CuHPO_3 + ZnHPO_3 (50:50)
- Mixture 3: CuHPO_3 + MnHPO_3 (50:50)
- Mixture 4: CuHPO_3 + MnHPO_3 (66:33)
- Mixture 100: Mixture 1 + IR5885 ($750^{(1)}$: $15^{(2)}$)
- 15 • Mixture 103: Mixture 3 + IR5885 ($750^{(1)}$: $15^{(2)}$)
- Mixture 105: Mixture 2 + IR5885 ($750^{(1)}$: $15^{(2)}$)
- Mixture 124: CuHPO_3 + IR5885 ($750^{(1)}$: $15^{(2)}$)
- Mixture 125: CuHPO_3 + IR6141 ($750^{(1)}$: $15^{(2)}$)
- Mixture 126: Mixture 1 + IR6141 ($750^{(1)}$: $15^{(2)}$)
- 20 • Mixture 129: Mixture 3 + IR6141 ($750^{(1)}$: $15^{(2)}$)
- Mixture 131: Mixture 2 + IR6141 ($750^{(1)}$: $15^{(2)}$)
- Mixture 143: CuHPO_3 + $\text{Cu}(\text{SA})$ ($750^{(1)}$: $64^{(3)}$)
- Mixture 144: Mixture 1 + $\text{Cu}(\text{SA})$ ($750^{(1)}$: $64^{(3)}$)
- Mixture 145: Mixture 3 + $\text{Cu}(\text{SA})$ ($750^{(1)}$: $64^{(3)}$)
- 25 • Mixture 146: Mixture 2 + $\text{Cu}(\text{SA})$ ($750^{(1)}$: $64^{(3)}$)

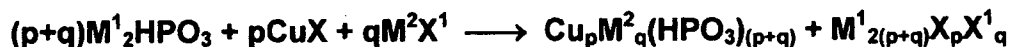
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- Mixture 152: $\text{CuHPO}_3 + \text{Cu(ASA)}_2$ (750⁽¹⁾:64⁽³⁾)
 - Mixture 153: Mixture 1 + Cu(ASA)_2 (750⁽¹⁾:64⁽³⁾)
 - Mixture 154: Mixture 3 + Cu(ASA)_2 (750⁽¹⁾:64⁽³⁾)
 - Mixture 155: Mixture 2 + Cu(ASA)_2 (750⁽¹⁾:64⁽³⁾)
 - 5 • Mixture 361: $\text{CuHPO}_3 + \text{Saccharin}$ (750⁽¹⁾:125⁽²⁾)
 - Mixture 362: Mixture 1 + Saccharin (750⁽¹⁾:125⁽²⁾)
 - Mixture 363: Mixture 2 + Saccharin (750⁽¹⁾:125⁽²⁾)
 - Mixture 364: Mixture 3 + Saccharin (750⁽¹⁾:125⁽²⁾)
10. The fungicidal composition according to claim 9,
10 characterized in that it consists of a mixture selected from mixture 1, mixture 2, mixture 3 and mixture 4.
11. A process for the preparation of a composition according to claim 1, characterized in that the mix-
15 tures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid are obtained by mixing the single salts or by co-precipitation of said salts in the reaction mixture.
- 20 12. The process according to claim 11, characterized in that the co-precipitation of the salts is effected starting from phosphites, for example sodium, potassium, by the shifting of the metallic cation M^1 with a mixture, in aqueous solution, of a copper (II)
25 salt and the other desired metallic salt, according

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to scheme A:

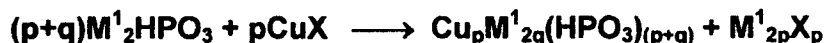
Scheme A



wherein M^1 represents a sodium or potassium atom, X represents a halogen, such as chlorine, bromine, iodine or a sulfate group, X^1 has the same meaning as X, M^2 represents an alkaline earth metal, an ammonium group or a Fe, Mn, Zn, Ni, Al, Ti, Se atom; p is a number greater than 0 and lower than 100 and q is equal to 100-p.

13. The process according to claim 11, characterized in that the co-precipitation of a copper (II) salt of phosphorous acid and a salt of an alkaline metal of phosphorous acid is effected starting from the above alkaline salt of phosphorous acid by partial shifting of the metallic cation with a suitable copper (II) salt according to scheme B:

Scheme B



wherein M^1 , X, p and q have the meanings indicated above.

14. The process according to claim 11, characterized in that the active substance, i.e. the copper (II) salt of phosphorous acid, and other metallic salts of phosphorous acid and/or the fungicidal compounds, is

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diluted or dissolved in a solvent medium and/or a solid diluent, possibly in the presence of surface-active agents.

15. The use of a fungicidal compound consisting of mix-
5 tures comprising a copper (II) salt of phosphorous acid and at least another metallic salt of phosphorous acid or mixtures comprising a copper (II) salt of phosphorous acid, alone or mixed with at least another metallic salt of phosphorous acid, and one
10 or more fungicidal compounds, for the control of phytopathogen fungi.
16. Use according to claim 15, characterized in that the phytopathogens are: Plasmopara viticola (vines);
Phytophthora infestans (tomatoes, pota-
15 toes); Phytophthora nicotianae (tobacco, ornamental plants); Phytophthora palmivora (cacao); Phytophthora cinnamomi (pineapples, citrus fruit); Phytophthora capsici (peppers, tomatoes, cucurbits); Phytophthora cryptogea (tomatoes, plums, ornamental plants); Phy-
20 tophthora megasperma (ornamental plants); Phytophthora citri (citrus fruit); Peronospora tabacina (tabacco); Pseudoperonospora cubensis (cauliflowers, cucurbits); Pseudoperonospora umili (hops); Phytoph-
25 tora cactorum (fruit trees); Phytophthora destructor (onions); Phytophthora fragariae (strawberries); Bre-

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mia (salad).

17. A method for the control of phytopathogen fungi in agricultural crops by the application of a fungicidal composition according to one of the claims 1-
5 10.
18. The method according to claim 17, characterized in that the fungicidal composition has the following application dosages per hectare:
- 1,000-4,000 g of salt of phosphorous acid;
 - 10 - 5-3,500 g for each fungicidal compound from (1) to (34) present in the composition.
19. The method according to claim 17, characterized in that the application is effected on all parts of the plant, for example on the leaves, stems, branches
15 and roots, or on the seeds themselves before sowing, or on the ground in which the plant grows.
20. The method according to claim 17, characterized in that the application is effected for preventive, protective, prophylactic, systemic, curative and de-
20 rooting treatment.

PATENT COOPERATION TREATY

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From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT AND
THE WRITTEN OPINION OF THE INTERNATIONAL
SEARCHING AUTHORITY, OR THE DECLARATION

To:

BARZANO' & ZANARDO MILANO S.P.A.
Attn. De Gregori, Antonella
Via Borgonuovo, 10
I-20121 Milan
ITALIE

(PCT Rule 44.1)

Date of mailing
(day/month/year) 12/01/2007

Applicant's or agent's file reference

NdP/91344

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.

PCT/EP2006/005157

International filing date
(day/month/year)

29/05/2006

Applicant

ISAGRO S.P.A.

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally two months from the date of transmittal of the International Search Report.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
1211 Geneva 20, Switzerland, Fascimile No.: (41-22) 338.82.70

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

- ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.
☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Reminders

Shortly after the expiration of 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

Within 19 months from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later); otherwise, the applicant must, within 20 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of 30 months (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Sandrine Parriche

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report and the written opinion of the International Searching Authority, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only (see *PCT Applicant's Guide*, Volume I/A, Annexes B1 and B2).

The attention of the applicant is drawn to the fact that amendments to the claims under Article 19 are not allowed where the International Searching Authority has declared, under Article 17(2), that no international search report would be established (see *PCT Applicant's Guide*, Volume I/A, paragraph 296).

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments and any accompanying statement, under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the time of filing the amendments (and any statement) with the International Bureau, also file with the International Preliminary Examining Authority a copy of such amendments (and of any statement) and, where required, a translation of such amendments for the procedure before that Authority (see Rules 55.3(a) and 62.2, first sentence). For further information, see the Notes to the demand form (PCT/IPEA/401).

If a demand for international preliminary examination is made, the written opinion of the International Searching Authority will, except in certain cases where the International Preliminary Examining Authority did not act as International Searching Authority and where it has notified the International Bureau under Rule 66.1bis(b), be considered to be a written opinion of the International Preliminary Examining Authority. If a demand is made, the applicant may submit to the International Preliminary Examining Authority a reply to the written opinion together, where appropriate, with amendments before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later (Rule 43bis.1(c)).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see the *PCT Applicant's Guide*, Volume II.

PATENT COOPERATION TREATY

PCT

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference NdP/91344	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/EP2006/005157	International filing date (day/month/year) 29/05/2006	(Earliest) Priority Date (day/month/year) 31/05/2005
Applicant ISAGRO S.P.A.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 6 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of:



the international application in the language in which it was filed



a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

2. ☐ Certain claims were found unsearchable (See Box No. II)

3. ☒ Unity of invention is lacking (see Box No III)

4. With regard to the title,



the text is approved as submitted by the applicant



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the drawings,

a. the figure of the drawings to be published with the abstract is Figure No. _____



as suggested by the applicant



as selected by this Authority, because the applicant failed to suggest a figure



as selected by this Authority, because this figure better characterizes the invention

b. ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2006/005157

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Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-10, 15-20

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-10, 15-20

Pesticidal composition comprising a mixture of copper (II) phosphite and at least another metallic phosphite or at least another fungicidal compound or at least another metallic phosphite and at least another fungicidal compound

2. claims: claim 11-14

Process for providing a mixture of cupric phosphite and at least another metallic phosphite.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/005157

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01N59/26

ADD. A01N59/20 A01N25/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 230 209 A2 (CIBA GEIGY AG [CH]) 29 July 1987 (1987-07-29)	1-10, 15-20
Y	last paragraph page 2 - page 3; claim 8 last paragraph page 4 - page 6 1st paragraph page 7	1-10, 15-20
X	----- US 4 075 324 A (THIZY ANDRE ET AL) 21 February 1978 (1978-02-21) cited in the application	1-5, 15-20
Y	column 6, line 31 - column 7, line 59; example 2 column 8, lines 31-43 claims 9,13 ----- -/-	1-10, 15-20

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

16 November 2006

Date of mailing of the international search report

12.01.07

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/005157

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/047540 A2 (ISAGRO SPA [IT]; GARAVAGLIA CARLO [IT]; MIRENNA LUIGI [IT]; OSTI SAMUE) 10 June 2004 (2004-06-10) page 1, lines 9-17 page 2, line 10 - page 7, line 10 -----	1-10, 15-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/005157

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PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

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To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/EP2006/005157

International filing date (day/month/year)
29.05.2006

Priority date (day/month/year)
31.05.2005

International Patent Classification (IPC) or both national classification and IPC
INV. A01N59/26
ADD. A01N59/20 A01N25/00

Applicant
ISAGRO S.P.A.

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

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Date of completion of
this opinion

see form
PCT/ISA/210

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**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

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Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:
 - ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material:
 - ☐ a sequence listing
 - ☐ table(s) related to the sequence listing
 - b. format of material:
 - ☐ on paper
 - ☐ in electronic form
 - c. time of filing/furnishing:
 - ☐ contained in the international application as filed.
 - ☐ filed together with the international application in electronic form.
 - ☐ furnished subsequently to this Authority for the purposes of search.
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

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Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of

☐ the entire international application

☒ claims Nos. 1-20

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international search (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed (*specify*):

☒ no international search report has been established for the whole application or for said claims Nos. 1-20

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.

☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.

☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13ter.1(a) or (b).

☐ a meaningful opinion could not be formed without the tables related to the sequence listings; the applicant did not, within the prescribed time limit, furnish such tables in electronic form complying with the technical requirements provided for in Annex C-bis of the Administrative Instructions, and such tables were not available to the International Searching Authority in a form and manner acceptable to it.

☐ the tables related to the nucleotide and/or amino acid sequence listing, if in electronic form only, do not comply with the technical requirements provided for in Annex C-bis of the Administrative Instructions.

☐ See Supplemental Box for further details

**WRITTEN OPINION OF THE
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Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has, within the applicable time limit:
- ☐ paid additional fees
 - ☐ paid additional fees under protest and, where applicable, the protest fee
 - ☐ paid additional fees under protest but the applicable protest fee was not paid
 - ☒ not paid additional fees
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is
- ☐ complied with
 - ☒ not complied with for the following reasons:
see separate sheet
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☐ all parts.
 - ☒ the parts relating to claims Nos. 1-10, 15-20

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	
	No: Claims	1-10, 15-20
Inventive step (IS)	Yes: Claims	
	No: Claims	1-10, 15-20
Industrial applicability (IA)	Yes: Claims	1-10, 15-20
	No: Claims	

2. Citations and explanations

see separate sheet

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

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Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Re Item IV.

The present application is directed to a fungicidal composition (claims 1-10) and its use (claims 15-20) as well as to a process for the preparation of a mixture of cupric phosphite and at least another metallic phosphite (claims 11-14).

The claimed matter is not so linked as to form a single general inventive concept (Rule 13.1 PCT) for the following reasons.

There are two problems to be solved a priori:

- (1) the provision of synergistic compositions comprising cupric phosphite
- (2) the provision of a process for providing a mixture of cupric phosphite and at least another metallic phosphite.

The solution to the first problem is a composition consisting of a mixture of cupric phosphite to at least another fungicide selected between at least one metallic phosphite, one or more fungicidal compounds, at least another metallic phosphite and one or more fungicidal compounds.

The solution to the second problem consists in a process comprising mixing the single salts co-precipitating said salts according to Scheme A or Scheme B.

The solutions to solve the first problem (the composition) cannot solve the second problem and viceversa.

Therefore, the ISA has identified the following two (groups of) inventions:

- (1) claims 1-10,15-20: Provision of synergistic compositions comprising CuHPO_3 ;
- (2) claims 11-14: Provision of a process for the preparation of a mixture of CuHPO_3 and at least one metallic salt of phosphorous acid.

These are not linked to form a single inventive concept in the meaning of Rules 13.1 and 13.2 PCT.

Furthermore, the ISA notes that also the first group of inventions is not unitary, as explained below.

The common concept of the first group of invention is the provision of synergistic fungicidal compositions comprising cupric phosphite.

The solution proposed in claim 1 is a composition consisting of mixtures comprising cupric phosphite and an additional fungicide selected from at least another metallic phosphite and/or one or more fungicidal compounds

Synergistic compositions containing Cu(II) phosphite and another fungicidal compound are known, for example from EP-A2-0 230 209. This document discloses synergistic fungicidal compositions comprising an acylalanine-type of fungicide ("Wirkstoff I") and a fungicide ("Wirkstoff II") selected from phosphorous acid, an ammonium phosphite, a phosphite salt of an alkaline or earth-alkaline metal or Zn, Cu, Ni or Mn. CuHPO_3 is one of the preferred compounds (compound (n), p.7, 1st paragraph). In particular, combinations of cupric

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phosphite and the preferred compounds Metalaxyl, Benalaxyl, Ofurace and Oxadixyl are already disclosed (see pp.5-6 and p.7, last paragraph). Thus, the novelty of at least claim 1 is anticipated by said document.

The distinguishing feature of the claims on file over EP-A2-0 230 209 is the compound that synergizes with the cupric phosphite, namely

(1) at least another metallic phosphite

(2)-(35) each of compounds (1) to (34) recited in claim 5.

Each of these compounds are different from one another, therefore, there is no common feature shared among the proposed solutions.

For reasons of efficiency, the ISA has decided not to request the fees for this further subgroup of inventions. However, a further objection of lack of unity of invention could be raised at a later stage, e.g. upon entry in the European phase.

The Applicant has declined the invitation to pay additional search fees for the additional groups of invention. The present opinion is therefore restricted to the subject-matter for which a search report has been established, namely, claims 1-10, 15-20.

Re Item V

The following documents are referred to:

D1: EP-A2-0 230 209(1987-07-29)

D2: US-A-4 075 324(1978-02-21) cited in the application

D3: WO 2004/047540 (2004-06-10)

Novelty

1/

The present application does not meet the requirements of Art.33(2)PCT because the subject-matter on file is not novel over D1.

Document D1 discloses synergistic fungicidal compositions comprising an acylalanine-type of fungicide ("Wirkstoff I") and a fungicide ("Wirkstoff II") selected from phosphorous acid, an ammonium phosphite, a phosphite salt of an alkaline or earth-alkaline metal or Zn, Cu, Ni or Mn. Cupric phosphite is one of the preferred compounds (p.7, of 1st paragraph, compound (n)). Thus, synergistic combinations of cupric phosphite and one fungicidal acylalanine are anticipated by D1.

Furthermore, combinations of cupric phosphite and any of the preferred compounds listed on pp.5-6 such as Metalaxyl, Benalaxyl, Ofurace and Oxadixyl are as well disclosed in D1. It follows that claims 1, 5, 15-20 are anticipated by D1.

Since it is not required from the wording of claims 2-4, 6-8 that the at least one metallic salt of phosphorous acid is present in the mixture (see clarity objection below), said claims still cover the embodiment anticipated by D1. Thus, these are formally not novel.

2/

D2 and D3 are not relevant to the novelty of the application.

D2 discloses a fungicidal composition containing CuHPO₃ (compound 13) and its fungicidal effect (example 2 columns 6-7), but there are no examples of fungicidal mixtures with CuHPO₃ and additional fungicide(s).

Document D3 does not disclose fungicidal compositions comprising CuHPO₃.

Inventive Step

The present application does not meet the requirements of Art.33(3) as explained below.

1/

The problem to be solved by the application is the provision of synergistic fungicidal compositions comprising cupric phosphite.

The solution proposed in claim 1 is a composition consisting of mixtures comprising cupric phosphite (CuHPO₃) and at least another metallic phosphite and/or one or more additional fungicide.

2/

The scope of claim 1 covers mixtures of CuHPO₃ with any thinkable fungicidal component. This covers thousands of mixtures. It is not credible that each and every of these mixtures provides a synergistic effect. Therefore, there are serious doubts that the problem is solved over the whole breadth of the claims (Art.33(3)PCT).

3/

As discussed above, D1 already discloses combinations of CuHPO₃ and acylalanine-type of fungicides. Furthermore, on p.14, last paragraph, of D1 it is mentioned that the compositions disclosed can contain an additional ingredient selected from copper sulphate or oxychloride, Zineb, Maneb, Propineb, Mancozeb, Folpet, Captan, Captafol, Chlorothalonil, Dithianon, Dichlofluanid, Chloroneb or Hymexazol.

Thus, an inventive step for claims 1,5,15-20 cannot be acknowledged.

4/

The claimed matter 1-10,15-20 lacks of inventive step over D2.

Document D2 a method of controlling fungus disease in plants comprising applying to said plants a fungicidally effective amount of **at least one compound** selected from the group consisting of alkali metal salt, ammonium salt, alkaline earth salt and the salt of a heavier metal selected from the group consisting of **copper**, iron, nickel, cobalt, manganese, zinc and aluminum. CuHPO₃ is exemplified in example 13, column 3 and is tested in Example 2, in comparison with other phosphites (compounds 1-12,14-25).

At the end of the example 2, it is concluded that some of the tested compounds, more

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especially the water-soluble salts, show better systemic properties than the substantially insoluble salts. By contrast, the substantially insoluble salts are more persistent in their effect. It is for this reason that **it is possible with advantage to mix these products with one another, more especially with a soluble compound and a less soluble compound so as to combine protection of seedlings with high persistence.**

Therefore, it is suggested in D2 to mix CuHPO_3 (low solubility) with a water-soluble phosphite among compounds 1-12, 14-25 tested in the examples or with one of the fungicides cited in column 8. The fact that for some of the mixtures it is shown in the application that synergy occurs, is only an additional benefit deriving from an obvious choice.

D2 teaches (column 8, lines 32-42) also that the compounds therein disclosed may be used with advantage in **admixture with one another (thus as mixtures) or with other known fungicides**, such as maneb, zineb, mancozeb, basic salts or hydroxides of copper (oxychloride, oxysulphate), captane, captafol, folpel, N-(1-butyl carbamoyl)-2-benzimidazole, benomyl, thiophanates, methyl 2-benzimidazole carbamate, either to complete the range of activity of the compounds according to the invention or to increase their persistence. In the absence of data showing a synergistic effect, it is considered obvious to combine CuHPO_3 with any of the above cited pesticides.

5/

The subject-matter of claims 1-10, 15-20 is not inventive over D3 in combination with either D1 or D2.

Document D3 discloses synergistic fungicidal compositions consisting of mixtures comprising A) at least one salt of an alkaline or alkaline-earth metal, Mn or Zn of phosphorous acid and B) at least a second fungicidal component. In particular, the fungicidal component B) can be selected from compounds (1)-(45) listed in claim 2.

Documents D1 and D2, respectively, disclose that CuHPO_3 is a fungicidal compound. In view of D1 or D2, selecting CuHPO_3 as additional fungicide to the synergistic mixtures disclosed in D3 is considered obvious, unless evidence is provided that this results in unexpected effects (a stronger synergy?).

Re Point VII (Clarity)

Claim 1 covers three alternative embodiments:

- (a) mixtures comprising cupric phosphite and at least another metallic phosphite
- (b) mixtures comprising cupric phosphite and at least an additional fungicide
- (c) mixtures comprising cupric phosphite and at least another metallic phosphite and at least an additional fungicide.

For the sake of clarity, each embodiment should be claimed separately.

COMPOSICIONES FUNGICIDAS SINÉRGICAS

La presente invención se relaciona con composiciones fungicidas sinérgicas. En particular, la presente invención se relaciona con nuevas composiciones sinérgicas capaces de controlar fitopatógenos que causan considerables daños económicos a la agricultura.

De manera más específica, la presente invención también se relaciona con el uso de composiciones que comprenden mezclas basadas en una sal cúprica (II) del ácido fosforoso, también llamada fosfito o fosfonato, con por lo menos otra sal metálica del ácido fosforoso, el uso de composiciones que comprenden mezclas basadas en una sal cúprica (II) del ácido fosforoso, también llamada fosfito o fosfonato, sola o mezclada con por lo menos otra sal metálica del ácido fosforoso, y uno o más compuestos fungicidas.

El uso de sales del ácido fosforoso como fungicidas es generalmente conocido en la bibliografía como, por ejemplo en la patente estadounidense US 4.075.324.

El Solicitante ha encontrado ahora de forma sorprendente que las sales cúpricas (II) del ácido fosforoso son capaces de ejercer un efecto sinérgico considerable que permite la obtención de una mayor actividad fungicida de la que es de prever con base en las actividades de componentes únicos, cuando se aplican en composición con otros fungicidas, además de proporcionar excelentes propiedades anti-resistencia.

Dado que los fenómenos de resistencia pueden surgir en la naturaleza como resultado del tratamiento prolongado con fungicidas sistémicos, siempre es importante y necesario encontrar sinergias orientadas hacia estrategias anti-resistencia.

De manera más específica, el Solicitante ha encontrado ahora de forma sorprendente que las mezclas basadas en las sales cúpricas (II) del ácido fosforoso y una o más sales del ácido fosforoso obtenidas de metales diferentes del cobre, tienen un efecto sinérgico considerable, que permite obtener una mayor actividad fungicida de la que sería de prever con base en las actividades de los single componentes únicos y capaces de controlar de forma efectiva numerosas enfermedades que pueden causar daño a los cultivos de gran interés económico como las vides, las papas y el tabaco.

Las mencionadas mezclas también tienen un excelente perfil toxicológico y ambiental, así como la ventaja de una gama más amplia de usos que permite reducir las dosificaciones de uso del cobre y también, posiblemente, del ácido fosforoso.

Además, el Solicitante de forma sorprendente ha encontrado que las mezclas mencionadas de fosfito de cobre (II) y otros fosfitos metálicos, en adición al fosfito de cobre (II) solo, a su vez demuestran una significativa sinergia con numerosos productos

fungicidas, que tienen dianas biológicas comunes con las de la mencionada sal cúprica (II) del ácido fosforoso.

Uno de los objetos de la presente invención por tanto se relaciona con una composición fungicida compuesta por de mezclas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso o compuestas por mezclas que comprenden una sal cúprica (II) del ácido fosforoso, sola o mezclada con por lo menos otra sal metálica del ácido fosforoso, y uno o más compuestos fungicidas.

En particular, la sal metálica del ácido fosforoso puede ser una sal de un metal alcalino, un metal alcalinotérreo, una sal de amonio o una sal de Fe, Mn, Zn, Ni, Al, Ti o Se. Dentro del espíritu de la presente invención, las mezclas mencionadas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso, se pueden obtener bien sea mezclando las sales solas, o mediante la precipitación conjunta de las sales mencionadas en una mezcla de reacción; en ambos casos, en la anterior mezcla, la sal cúprica (II) del ácido fosforoso y las otras sales metálicas del ácido fosforoso pueden estar presentes en cualquier proporción, estado de solvatación, estructura o composición de la red cristalina.

Las sales de metal alcalino, metal alcalinotérreo, sal de amonio o sales de Fe, Mn, Zn, Ni, Al, Ti o Se, del ácido fosforoso pueden ser mono-o bibásicas, o pueden ser mezclas de éstas en cualquier proporción.

En las composiciones fungicidas conforme a la presente invención, las mezclas mencionadas también pueden contener sales de metales alcalinos en porcentajes no superiores al 10% en peso, como sales de intercambio de reacción que no obstante no tienen una actividad fungicida directa.

Como ya se dijo, una extensión del mencionado concepto de la sinergia es la obtención de mezclas que comprenden una sal cúprica (II) del ácido fosforoso sola o en una mezcla con por lo menos otra sal metálica del ácido fosforoso, con otros compuestos fungicidas que tienen dianas biológicas comunes con las de la mencionada sal cúprica (II) del ácido fosforoso.

El compuesto que tiene una actividad fungicida conforme a la presente invención de preferencia se selecciona de entre:

- (1) IR5885, un el compuesto dipeptídico que corresponde una mezclas diastereoisoméricas de propanoato de metil [S-(R,S)]-[3-(N-isopropoxycarbonilvalinil)-amino]-3-(4-cloro-fenil) en cualquier proporción, o a una de las dos formas diastereoisoméricas S-R o S-S tomadas individualmente;
- (2) IR6141, que corresponde a alaninato de N-(fenilacetil)-N-2,6-xilil-R-metilo;

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- (3) Ácido salicílico (SA) o sus derivados como ácido acetilsalicílico (ASA), sales cúpricas del ácido salicílico o del ácido acetilsalicílico;
- (4) A cobre (I) o sal cúprica (II), como oxiclورو de cobre, hidróxido de cobre, mezcla de Burdeos, sulfato de cobre, o una mezcla de hidróxido y oxiclورو de cobre (Airone);
- (5) Benalaxil que corresponde a alaninato de N-(fenilacetil)-N-2,6-xilil-RS-metilo;
- (6) Metalaxil que corresponde a alaninato de N-(2-metoxiacetil)-N-2,6-xilil-RS-metilo;
- (7) Metalaxil-M que corresponde a alaninato de N-(2-metoxiacetil)-N-2,6-xilil-R-metilo;
- (8) Oxadixilo que corresponde a 2-metoxi-N-(2-oxo-1,3-oxazolidin-3-il)aceto-2',6'-xilidato;
- (9) Ofurace que corresponde a DL-3-[N-cloroacetil-N-(2,6-xilil)-amino]- γ -butirolactona;
- (10) Iprovalicarb que corresponde a carbamato de O-(1-metil-etil)-N-[2-metil-1-[[[1-(4-metil-fenil)-etil]amino]carbonil]propilo];
- (11) Bentiavalicarb-isopropilo que corresponde a O-isopropil[(S)-1-{(IR)-1-(6-fluoro-1, 3-benzo-tiazol-2-il)etil-carbamoyl-2-metilpropil]-carbamato;
- (12) Cimoxanilo que corresponde a 1-(2-ciano-2-metoxiimino-acetil)-3-etilurea,
- (13) Azoxistrobin que corresponde a metoxiacrilato de (E)-2-[2-[6-(2-cianofenoxi)-pirimidin-4-iloxi] fenil-3-metilo];
- (14) Metominofén que corresponde a N-metil-(E)-metoxiimino-(2-fenoxifenil)acetamida;
- (15) Piraclostrobin que corresponde a metil N-(2-[1-(4-clorofenil)pirazol-3-iloximetil]-fenil)-N-metoxicarbamato;
- (16) Acibenzolar-S-metilo que corresponde a metil benzo(1,2,3)tiadiazol-7-tiocarboxilato;
- (17) Famoxadona que corresponde a 5-metil-5-(4-fenoxifenil)-3-(fenilamino)oxazolidin-2,4-diona;
- (18) Fenamidone que corresponde a 4-metil-4-fenil-1-(fenilamino)-2-metiltioimidazolidin-5-ona;
- (19) Ciazofamida, que corresponde a 2-ciano-4-cloro-5-(4-metilfenil)-1-(N,N dimetilaminosulfamoyl)-imidazol;
- (20) Fluzinam que corresponde a 3-cloro-N-(3-cloro-5-trifluorometil-2-piridil)- α - α -trifluoro-2, 6-dinitro-p-toluidina;
- (21) Dimetomorfo que corresponde a (E, Z)-4-[3-(4-clorofenil)-3-(3, 4-dimetoxifenil)-acriloyl] morfolina; o Flumorph (SYP-L190) que corresponde a (E, Z)-4-[3-(4-fluorofenil)-3-(3, 4-dimetoxi-fenil)-acriloyl] morfolina;

- (22) Flumetover que corresponde a 2-(3,4-dimetoxifenil)-N-etil- α,α,α -trifluoro-N-metil-p-toluamida;
- (23) Clorotalonilo que corresponde a 1,3-diciano-2,4,5-tetraclorobenceno;
- (24) Mancozeb que corresponde a la sal de manganeso y zinc de etilenebis(ditiocarbamato) (polímero);
- (25) Tolilfluanida que corresponde a N-dicloro-fluorometiltio-N',N'-dimetil-N-p-tolilsulf-amida;
- (26) Folpet que corresponde a N-(triclorometil-tio) ftalimida;
- (27) Etridiazole que corresponde a éter etil-3-triclorometil-1,2,4-tiadiazolílico;
- (28) Himexanol que corresponde a 5-metilisooxazol-3-ol;
- (29) Propamocarb que corresponde a carbamato de propil-(3-dimetilaminopropilo);
- (30) ácido R-3-aminobutanoico o ácido RS-3-aminobutanoico;
- (31) Zoxamida, que corresponde a 3, 5-dicloro-N-(3-cloro-1-etil-1-metil-2-oxopropil)-p-toluamida;
- (32) 2-(4-clorofenil)-N-[2-(3-metoxi-4-prop-2-iniloxi-fenil)etil]-2-prop-2-iniloxi-acetamida;
- (33) Etaboxam, (RS)-(α -ciano-2-tienil)-4-etil-2(etilatnino)-5-tiazolcarboxiamida,
- (34) Sacarina

Los compuestos (1) están descritos en la solicitud italiana de patente No. MI98A002583.

El compuesto (2) está descrito en la solicitud de patente WO 98/26654 A2.

Los compuestos (3) son productos comerciales y sus sales cúpricas están descritas en la solicitud italiana de patente No. MI 2001A002430.

Los compuestos (4) están fácilmente disponibles en el mercado.

El compuesto (5) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 32.

El compuesto (6) está descrito en la patente inglesa GB 1.500.581.

El compuesto (7) está descrito en la solicitud de patente WO 96/01559 A1.

El compuesto (8) está descrito en la patente inglesa GB 2.058.059.

El compuesto (9) está descrito en "Phytopathological News" (1978), Vol. 9, página 142.

El compuesto (10) está descrito en las solicitudes de patente EP 550.788EP 775.696.

El compuesto (11) está descrito en la solicitud de patente EP 775.696.

El compuesto (12) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 148.

El compuesto (13) está descrito en la solicitud europea de patente EP 382.375.

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El compuesto (14), que corresponde a la abreviatura experimental SSF-126, está descrito en la patente estadounidense 5.185.242.

El compuesto (15) está descrito en la solicitud de patente WO 96/01258.

El compuesto (16) está descrito en la patente estadounidense 4.931.581.

El compuesto (17) está descrito en "Brighton Crop Protection Conference – Pests and Diseases" 1996, Memorias del Congreso.

El compuesto (18) está descrito en la solicitud europea de patente EP 629.616.

El compuesto (19), también llamado IKF916, está descrito en la solicitud europea de patente EP 705.823.

El compuesto (20) está descrito en la solicitud europea de patente EP 31.257.

Los compuestos (21) están descritos respectivamente en la solicitud europea de patente EP 219,756 in "Brighton Crop Protection Conference - Pests and Diseases" 2000, Memorias del Congreso.

El compuesto (22) está descrito en las solicitudes europeas de patente EP 360.701 y EP 611.232.

El compuesto (23) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 120.

El compuesto (24) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 339.

El compuesto (25) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 537.

El compuesto (26) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 599.

El compuesto (27) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 252.

El compuesto (28) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 314.

El compuesto (29) está descrito en "The Pesticide Manual", 1983, VII edición, British Crop Protection Council Ed., página 471.

El compuesto (30) está descrito en la solicitud europea de patente EP 753,258.

El compuesto (31) está descrito en "Brighton Crop Protection Conference - Pests and Diseases" 1998, Memorias del Congreso.

El compuesto (32) está descrito en la solicitud de patente WO 01/87822.

El compuesto (33) está descrito en "The Pesticide Manual", 2003, XIII edición, British Crop Protection Council Ed.

El compuesto (34) es un producto comercial.

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Las composiciones fungicidas preferidas conforme a la presente invención se pueden seleccionar de entre:

- Mezcla 1: $\text{CuHPO}_3 + \text{CaHPO}_3$ (50:50)
- Mezcla 2: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (50:50)
- Mezcla 3: $\text{CuHPO}_3 + \text{MnHPO}_3$ (50:50)
- Mezcla 4: $\text{CuHPO}_3 + \text{MnHPO}_3$ (66:33)
- Mezcla 100: Mezcla 1 + IR5885 ($750^{(1)}$: $15^{(2)}$)
- Mezcla 103: Mezcla 3 + IR5885 ($750^{(1)}$: $15^{(2)}$)
- Mezcla 105: Mezcla 2 + IR5885 ($750^{(1)}$: $15^{(2)}$)
- Mezcla 124: $\text{CuHPO}_3 + \text{IR5885}$ ($750^{(1)}$: $15^{(2)}$)
- Mezcla 125: $\text{CuHPO}_3 + \text{IR6141}$ ($750^{(1)}$: $15^{(2)}$)
- Mezcla 126: Mezcla 1 + IR6141 ($750^{(1)}$: $15^{(2)}$)
- Mezcla 129: Mezcla 3 + IR6141 ($750^{(1)}$: $15^{(2)}$)
- Mezcla 131: Mezcla 2 + IR6141 ($750^{(1)}$: $15^{(2)}$)
- Mezcla 143: $\text{CuHPO}_3 + \text{Cu(SA)}$ ($750^{(1)}$: $64^{(3)}$)
- Mezcla 144: Mezcla 1 + Cu(SA) ($750^{(1)}$: $64^{(3)}$)
- Mezcla 145: Mezcla 3 + Cu(SA) ($750^{(1)}$: $64^{(3)}$)
- Mezcla 146: Mezcla 2 + Cu(SA) ($750^{(1)}$: $64^{(3)}$)
- Mezcla 152: $\text{CuHPO}_3 + \text{Cu(ASA)}_2$ ($750^{(1)}$: $64^{(3)}$)
- Mezcla 153: Mezcla 1 + Cu(ASA)_2 ($750^{(1)}$: $64^{(3)}$)
- Mezcla 154: Mezcla 3 + Cu(ASA)_2 ($750^{(1)}$: $64^{(3)}$)
- Mezcla 155: Mezcla 2 + Cu(ASA)_2 ($750^{(1)}$: $64^{(3)}$)
- Mezcla 361: $\text{CuHPO}_3 + \text{Sacarina}$ ($750^{(1)}$: $125^{(2)}$)
- Mezcla 362: Mezcla 1 + Sacarina ($750^{(1)}$: $125^{(2)}$)
- Mezcla 363: Mezcla 2 + Sacarina ($750^{(1)}$: $125^{(2)}$)
- Mezcla 364: Mezcla 3 + Sacarina ($750^{(1)}$: $125^{(2)}$)

(1): dosificación expresada en ppm de equivalentes de ácido fosforoso.

(2): dosificación expresada en ppm del ingrediente activo

(3): dosificación expresada en ppm de equivalentes de cobre metálico.

Las composiciones fungicidas definidas como mezcla 1, mezcla 2, mezcla 3 y mezcla 4 son especialmente preferidas.

Cuando no son productos comerciales, las sales metálicas solas del ácido fosforoso se pueden obtener fácilmente en solución acuosa mediante reacción del ácido fosforoso con una base inorgánica como el hidróxido o carbonato del metal deseado, o por reacción del ácido fosforoso con una base inorgánica, como hidróxido de sodio o potasio y la consiguiente reacción con una sal inorgánica como, por ejemplo, cloruro,

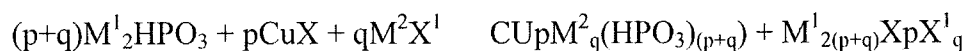
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bromuro o sulfato del metal deseado, como se describe en la bibliografía in: "GMelins Handbuch Der Anorganischen Chemie" Ed. Verlag Chemie-GMBH-Weinheim.

Las composiciones fungicidas conforme a la presente invención se pueden preparar como sigue: las mezclas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso se obtienen mezclando las sales solas o mediante precipitación conjunta de las mencionadas sales en la mezcla de reacción.

En este segundo caso, la precipitación conjunta la precipitación conjunta de las sales se lleva a efecto comenzando a partir de fosfitos como, por ejemplo fosfitos de sodio o potasio, por el desplazamiento del catión metálico M^1 con una mezcla, en solución acuosa, de una sal cúprica (II) y la otra sal metálica deseada, conforme al esquema A:

Esquema A



en donde M^1 representa un átomo de sodio o potasio, X representa un halógeno, como cloro, bromo, yodo o un grupo sulfato, X^1 tiene el mismo significado que X, M^2 representa un metal alcalinotérreo, un grupo amonio o un átomo de Fe, Mn, Zn, Ni, Al, Ti, Se; p es un número mayor de 0 y menor de 100 y q es igual a 100-p.

La precipitación conjunta de una sal cúprica (II) del ácido fosforoso y una sal de un metal alcalino del ácido fosforoso se lleva a efecto comenzando a partir de la anterior sal alcalina del ácido fosforoso mediante desplazamiento parcial del catión metálico con una sal cúprica apropiada (II) conforme al esquema B:

Esquema B



en donde M^1 , X, p y q tienen los significados arriba indicados. De manera análoga, se pueden preparar mezclas que comprenden, además de cobre, dos o más metales seleccionados de entre los enumerados arriba.

Las composiciones fungicidas conforme a la presente invención que comprenden:

a) una sal cúprica (II) de ácido fosforoso mezclada con por lo menos una sal de un metal alcalino, un metal alcalinotérreo, una sal de amonio o una sal de Fe, Mn, Zn, Ni, Al, Ti, Se del ácido fosforoso;

b) una sal cúprica (II) del ácido fosforoso sola o en una mezcla con por lo menos una sal de un metal alcalino, un metal alcalinotérreo, una sal de amonio, o una sal de Fe, Mn, Zn, Ni, Al, Ti, Se del ácido fosforoso, y por lo menos uno de los compuestos fungicidas (I)-(34);

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todos tienen una elevada actividad fungicida con respecto a numerosas especies de hongos.

Otro objeto de la presente invención por tanto tiene que ver con el uso de una composición compuesta de mezclas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso o el uso de una composición compuesta de mezclas basadas en una sal cúprica (II) del ácido fosforoso, sola o mezclada con por lo menos otra sal metálica del ácido fosforoso y uno o más compuestos fungicidas, en particular uno o más compuestos fungicidas (1)-(34), para el control de hongos fitopatógenos.

Un objeto de la presente invención también se relaciona con un método para el control de hongos fitopatógenos en agricultura mediante la aplicación de una composición fungicida compuesta por mezclas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso o por la aplicación de una composición compuesta de mezclas basadas en una sal cúprica (II) del ácido fosforoso solas o en una mezcla con por lo menos otra sal metálica de ácido fosforoso y uno o más compuestos fungicidas, en particular uno o más compuestos fungicidas (1)-(34).

A continuación se da una lista de algunos ejemplos de los patógenos que se controlan con las composiciones arriba mencionadas, junto con ejemplos de la aplicación a cultivos, para efectos puramente ilustrativos y no limitantes:

- Plasmopara viticola (vid);
- Phytophthora infestans (tomate, papa)
- Phytophthora nicotianae (tabaco, plantas ornamentales);
- Phytophthora palwivora (cacao);
- Phytophthora cinnamomi (piña, cítricos);
- Phytophthora capsici (pimiento, tomate, cucurbitáceas);
- Phytophthora cryptogea (tomate, ciruela, plantas ornamentales);
- Phytophthora megasperma (plantas ornamentales);
- Phytophthora citri (cítricos);
- Peronospora tabacina (tabaco);
- Pseudoperonospora cubensis (coliflor, cucurbitáceas);
- Pseudoperonospora umili (lúpulo);
- Phytophthora cactorum (frutales);
- Phytophthora destructor (cebolla);
- Phytophthora fragariae (fresa);
- Bremia (hortaliza).

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Las composiciones objeto de la presente invención son capaces de ejercer una elevada actividad fungicida sinérgica que permite llevar a cabo tratamientos preventivos, protectores, profilácticos, sistémicos, curativos y desarraigantes.

En las anteriores composiciones, la sal cúprica (II) del ácido fosforoso y las otras sales metálicas del ácido fosforoso de preferencia están presentes en una proporción que varía de 10/90 a 90/10 en equivalentes de ácido fosforoso.

Todavía más de preferencia, la sal cúprica (II) del ácido fosforoso y las otras sales metálicas del ácido fosforoso se encuentran presentes en una proporción de 50/50 en equivalentes de ácido fosforoso.

Las composiciones objeto de la presente invención se pueden usar en diferentes cantidades en relación con el cultivo, el patógeno, condiciones ambientales y tipo de formulación adoptada.

Las composiciones fungicidas conforme a la presente invención en general prevén las siguientes dosificaciones de aplicación por hectárea:

1,000-4,000 g de sal del ácido fosforoso;-5-3,500 g para cada fungicida de (1) a (34) presente en la composición.

La aplicación de las composiciones objeto de la presente invención se puede realizar en todas las partes de la planta como, por ejemplo sobre las hojas, tallos, ramas y raíces, o sobre las semillas mismas antes de sembrar, o sobre la tierra en la cual crece la planta.

Las composiciones conforme a la presente invención se pueden usar en la práctica agrícola en diversas formas como, por ejemplo: polvos secos, polvos de humedecer, concentrados emulsionantes, micro-emulsiones, pastas, granulados, soluciones, suspensiones, etc. La elección del tipo de composición dependerá del uso específico.

Las composiciones se preparan de formas conocidas, por ejemplo, diluyendo o disolviendo la sustancia activa con un medio solvente o un diluyente sólido, posiblemente en presencia de agentes surfactantes.

Los diluyentes sólidos o soportes que se pueden usar son: sílice, caolín, bentonita, talco, tierra de infusorios, dolomita, carbonato de calcio, magnesio, yeso, arcillas, silicatos sintéticos, atapulgita, sepiolita.

Los diluyentes líquidos que se pueden usar, son por ejemplo, además de agua, compuestos aromáticos (xiloles o mezclas de alquilbenzoles), parafinas (fracciones del petróleo), alcoholes (metanol, propanol, butanol, octanol, glicerina), aminas, amidas (N,N-dimetilformamida, N-metilpirrolidona), cetonas (ciclohexanona, acetona, acetofenona, isoforona, etilamilcetone), ácidos grasos (por ejemplo, aceites vegetales

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como aceite de colza, aceite de girasol), esteres (acetato de isobutilo, esteres metílicos de ácidos grasos obtenidos, por ejemplo, de la transesterificación de aceites vegetales).

Como agentes surfactantes se pueden usar sales de sodio, sales de calcio, trietanolamina o trietilamina de alquilsulfonatos, alquilaril sulfonatos, alquilfenoles polietoxilados, alcoholes grasos condensados con óxido de etileno, ácidos grasos polietoxilados, esteres de sorbitol polietoxilados, ligninosulfonatos.

Las composiciones también pueden contener aditivos especiales para efectos particulares como, por ejemplo, agentes adhesivos, como goma arábiga, alcohol polivinílico, polivinilpirrolidona.

En las composiciones fungicidas objeto de la presente invención la concentración de la sustancia activa varía entre 0.1% y 98% en peso, de preferencia de 0.5% a 90% en peso.

Cuando se desee, se pueden añadir otros principios activos compatibles a las composiciones objeto de la presente invención como, por ejemplo, fitoreguladores, antibióticos, herbicidas, insecticidas, fertilizantes. Los siguientes ejemplos se dan para efectos puramente ilustrativos y no limitantes de la presente invención.

Ejemplo 1:

Preparación de la sal cúprica y cálcica del ácido fosforoso (50:50). Mezcla 1.

350 g de H_3PO_3 y 350 mL de H_2O se cargan en un matraz de 6 L. Se añaden 563,5 g de KOH disueltos en 700 mL de H_2O previamente enfriada hasta cerca de 30°C gota a gota bajo agitación sobre un baño de hielo. Después de unos pocos minutos, la solución acuosa obtenida por disolución de 364 g de $CuCl_2 \cdot 2H_2O$ y 313,95 g de $CaCl_2 \cdot 2H_2O$ en 3500 mL de H_2O se añaden gota a gota. El precipitado azul-verde que se forma se deja bajo agitación durante 24 horas a temperatura ambiente, el matraz entonces se calienta llevando la temperatura ambiente hasta cerca de 80°C la mezcla se deja bajo agitación durante otras 4 horas aproximadamente. La mezcla caliente se filtra en un embudo de Buchner y el sólido se lava con 3500 mL de H_2O previamente calentada hasta cerca de 80°C. Después de secar en un horno, se obtienen 652 g del producto deseado.

Análisis elemental [% encontrado (teórico)] = Cu 20,9 (21,2); Ca 13,0 (13,4); P 20,5 (20,7).

Ejemplo 2:

Preparación de la sal cúprica y de zinc del ácido fosforoso (50:50). Mezcla 2.

350 g de H_3PO_3 y 350 mL de H_2O se cargan en un matraz de 6 L. Se añaden 563,5 g de KOH disueltos en 700 mL de H_2O previamente enfriada hasta cerca de 30°C gota a gota bajo agitación sobre un baño de hielo. Después de unos pocos minutos, la solución acuosa obtenida por disolución de 364 g de $CuCl_2 \cdot 2H_2O$ y 613,9 g de

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$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ en 3500 mL de H_2O se añade gota a gota. El precipitado azul que se forma se deja bajo agitación durante 24 horas a temperatura ambiente, el matraz entonces se calienta llevando la temperatura ambiente hasta cerca de 80°C y la mezcla se deja bajo agitación durante otras 4 horas aproximadamente. La mezcla caliente se filtra en un embudo de Buchner y el sólido se lava con 3500 mL de H_2O previamente calentada hasta cerca de 80°C . Después de secar en un horno, se obtienen 699 g del producto deseado.

Análisis elemental [% encontrado (teórico)] = Cu 18,6 (21,2); Zn 16,6 (13,4); P 18,4 (20,7); K 4,18 (0).

Ejemplo 3:

Preparación de la sal de cobre y manganeso del ácido fosforoso (50:50). Mezcla 3.

350 g de H_3PO_3 y 350 mL de H_2O se cargan en un matraz de 6 L. Se añaden 563.5 g de KOH disueltos en 700 mL de H_2O previamente enfriada hasta cerca de 30°C gota a gota bajo agitación sobre un baño de hielo. Después de unos pocos minutos, la solución acuosa obtenida por disolución de 364 g de $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ y 360.86 g de $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ en 3500 mL de H_2O se añade gota a gota. El precipitado azul que se forma se deja bajo agitación durante 24 horas a temperatura ambiente, el matraz entonces se calienta llevando la temperatura ambiente hasta cerca de 80°C y la mezcla se deja bajo agitación durante otras 4 horas aproximadamente. La mezcla caliente se filtra en un embudo de Buchner y el sólido se lava con 3500 mL de H_2O previamente calentada hasta cerca de 80°C . Después de secar en un horno, se obtienen 451.7 g del producto deseado.

Análisis elemental [% encontrado (teórico)] = Cu 20,3 (21,4); Mn 16,8 (18,5); P 20,0 (20,9); K 1,49 (0).

Ejemplo 4:

Preparación de la sal de cobre y manganeso del ácido fosforoso (66:33). Mezcla 4.

350 g de H_3PO_3 y 350 mL de H_2O se cargan en un matraz de 6 L. Se añaden 563.5 g de KOH disueltos en 700 mL de H_2O previamente enfriada hasta cerca de 30°C gota a gota bajo agitación sobre un baño de hielo. Después de unos pocos minutos, la solución acuosa obtenida por disolución de 480,4 g de $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ y 238.2 g de $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ en 3500 mL de H_2O se añade gota a gota. El precipitado azul que se forma se deja bajo agitación durante 24 horas a temperatura ambiente, el matraz entonces se calienta llevando la temperatura ambiente hasta cerca de 80°C y la mezcla se deja bajo agitación durante otras 4 horas aproximadamente. La mezcla caliente se filtra en un embudo de Buchner y el sólido se lava con 3500 mL de H_2O previamente calentada hasta cerca de 80°C . Después de secar en un horno, se obtienen 482 g del producto deseado.

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Análisis elemental [% encontrado (teórico)] = Cu 27,7 (28,2); Mn 10,9 (12,2); P 18,0 (20,9); K 0,97 (0).

Las siguientes mezclas se pueden obtener mediante un procedimiento análogo:

- Mezcla 5: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (34:66)*
- Mezcla 6: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (66:34)*
- Mezcla 7: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (25:75)*
- Mezcla 8: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (75:25)*
- Mezcla 9: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (90:10)*
- Mezcla 10: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (10:90)*
- Mezcla 11: $\text{CuHPO}_3 + \text{CaHPO}_3$ (34:66)*
- Mezcla 12: $\text{CuHPO}_3 + \text{CaHPO}_3$ (66:34)*
- Mezcla 13: $\text{CuHPO}_3 + \text{CaHPO}_3$ (25:75)*
- Mezcla 14: $\text{CuHPO}_3 + \text{CaHPO}_3$ (75:25)*
- Mezcla 15: $\text{CuHPO}_3 + \text{CaHPO}_3$ (90:10)*
- Mezcla 16: $\text{CuHPO}_3 + \text{CaHPO}_3$ (10:90)*
- Mezcla 17: $\text{CuHPO}_3 + \text{MnHPO}_3$ (34:66)*
- Mezcla 18: $\text{CuHPO}_3 + \text{MnHPO}_3$ (25:75)*
- Mezcla 19: $\text{CuHPO}_3 + \text{MnHPO}_3$ (75:25)*
- Mezcla 20: $\text{CuHPO}_3 + \text{MnHPO}_3$ (90:10)*
- Mezcla 21: $\text{CuHPO}_3 + \text{MnHPO}_3$ (10:90)*
- Mezcla 22: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (50:50)*
- Mezcla 23: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (34:66)*
- Mezcla 24: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (66:34)*
- Mezcla 25: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (25:75)*
- Mezcla 26: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (75:25)*
- Mezcla 27: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (90:10)*
- Mezcla 28: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3$ (10:90)*
- Mezcla 29: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (50:50)*
- Mezcla 30: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (34:66)*
- Mezcla 31: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (66:34)*
- Mezcla 32: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (25:75)*
- Mezcla 33: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (75:25)*
- Mezcla 34: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (90:10)*
- Mezcla 35: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3$ (10:90)*
- Mezcla 36: $\text{CuHPO}_3 + \text{NiHPO}_3$ (50:50)*
- Mezcla 37: $\text{CuHPO}_3 + \text{NiHPO}_3$ (34:66)*
- Mezcla 38: $\text{CuHPO}_3 + \text{NiHPO}_3$ (66:34)*

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- Mezcla 39: $\text{CuHPO}_3 + \text{NiHPO}_3$ (25:75)*
- Mezcla 40: $\text{CuHPO}_3 + \text{NiHPO}_3$ (75:25)*
- Mezcla 41: $\text{CuHPO}_3 + \text{NiHPO}_3$ (90:10)*
- Mezcla 42: $\text{CuHPO}_3 + \text{NiHPO}_3$ (10:90)*
- Mezcla 43: $\text{CuHPO}_3 + \text{MgHPO}_3$ (50:50)*
- Mezcla 44: $\text{CuHPO}_3 + \text{MgHPO}_3$ (34:66)*
- Mezcla 45: $\text{CuHPO}_3 + \text{MgHPO}_3$ (66:34)*
- Mezcla 46: $\text{CuHPO}_3 + \text{MgHPO}_3$ (25:75)*
- Mezcla 47: $\text{CuHPO}_3 + \text{MgHPO}_3$ (75:25)*
- Mezcla 48: $\text{CuHPO}_3 + \text{MgHPO}_3$ (90:10)*
- Mezcla 49: $\text{CuHPO}_3 + \text{MgHPO}_3$ (10:90)*
- Mezcla 50: $\text{CuHPO}_3 + \text{BaHPO}_3$ (50:50)*
- Mezcla 51: $\text{CuHPO}_3 + \text{BaHPO}_3$ (34:66) *
- Mezcla 52: $\text{CuHPO}_3 + \text{BaHPO}_3$ (66:34) *
- Mezcla 53: $\text{CuHPO}_3 + \text{BaHPO}_3$ (25:75)*
- Mezcla 54: $\text{CuHPO}_3 + \text{BaHPO}_3$ (75:25)*
- Mezcla 55: $\text{CuHPO}_3 + \text{BaHPO}_3$ (90:10) *
- Mezcla 56: $\text{CuHPO}_3 + \text{BaHPO}_3$ (10:90) *
- Mezcla 57: $\text{CuHPO}_3 + \text{K}_2\text{HPO}_3$ (50:50)*
- Mezcla 58: $\text{CuHPO}_3 + \text{K}_2\text{HPO}_3$ (34:66) *
- Mezcla 59: $\text{CuHPO}_3 + \text{K}_2\text{HPO}_3$ (66:34)*
- Mezcla 60: $\text{CuHPO}_3 + \text{K}_2\text{HPO}_3$ (25:75)*
- Mezcla 61: $\text{CuHPO}_3 + \text{K}_2\text{HPO}_3$ (75:25)*
- Mezcla 62: $\text{CuHPO}_3 + \text{K}_2\text{HPO}_3$ (90:10)*
- Mezcla 63: $\text{CuHPO}_3 + \text{K}_2\text{HPO}_3$ (10:90)*
- Mezcla 64: $\text{CuHPO}_3 + (\text{NH}_4)_2\text{HPO}_3$ (50:50) *
- Mezcla 65: $\text{CuHPO}_3 + (\text{NH}_4)_2\text{HPO}_3$ (34:66) *
- Mezcla 66: $\text{CuHPO}_3 + (\text{NH}_4)_2\text{HPO}_3$ (66:34)*
- Mezcla 67: $\text{CuHPO}_3 + (\text{NH}_4)_2\text{HPO}_3$ (25:75) *
- Mezcla 68: $\text{CuHPO}_3 + (\text{NH}_4)_2\text{HPO}_3$ (75:25) *
- Mezcla 69: $\text{CuHPO}_3 + (\text{NH}_4)_2\text{HPO}_3$ (90:10)*
- Mezcla 70: $\text{CuHPO}_3 + (\text{NH}_4)_2\text{HPO}_3$ (10:90)*
- Mezcla 71: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (50:50) *
- Mezcla 72: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (34:66) *
- Mezcla 73: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (66:34)*
- Mezcla 74: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (25:75)*
- Mezcla 75: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (75:25)*

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- Mezcla 76: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (90:10)*
- Mezcla 77: $\text{CuHPO}_3 + \text{Ti}(\text{HPO}_3)_2$ (10:90)*
- Mezcla 78: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (50:50)*
- Mezcla 79: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (34:66)*
- Mezcla 80: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (66:34)*
- Mezcla 81: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (25:75)*
- Mezcla 82: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (75:25)*
- Mezcla 83: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (90:10)*
- Mezcla 84: $\text{CuHPO}_3 + \text{Se}(\text{HPO}_3)_2$ (10:90)*
- Mezcla 85: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{MnHPO}_3$ (34: 33: 33) *
- Mezcla 86: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{MnHPO}_3$ (50: 25: 25) *
- Mezcla 87: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{ZnHPO}_3$ (34: 33: 33) *
- Mezcla 88: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{ZnHPO}_3$ (50: 25: 25) *
- Mezcla 89: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{MnHPO}_3$ (34: 33: 33)*
- Mezcla 90: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{MnHPO}_3$ (50: 25: 25) *
- Mezcla 91: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{K}_2\text{HPO}_3$ (34: 33: 33)*
- Mezcla 92: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{K}_2\text{HPO}_3$ (50: 25: 25) *
- Mezcla 93: $\text{CuHPO}_3 + \text{CaHPO}_3 + \text{K}_2\text{HPO}_3$ (25: 25: 50) *
- Mezcla 94: $\text{CuHPO}_3 + \text{MnHPO}_3 + \text{K}_2\text{HPO}_3$ (34: 33: 33) *
- Mezcla 95: $\text{CuHPO}_3 + \text{MnHPO}_3 + \text{K}_2\text{HPO}_3$ (50: 25: 25) *
- Mezcla 96: $\text{CuHPO}_3 + \text{MnHPO}_3 + \text{K}_2\text{HPO}_3$ (25: 25: 50) *
- Mezcla 97: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{K}_2\text{HPO}_3$ (34: 33: 33) *
- Mezcla 98: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{K}_2\text{HPO}_3$ (50: 25: 25) *
- Mezcla 99: $\text{CuHPO}_3 + \text{ZnHPO}_3 + \text{K}_2\text{HPO}_3$ (25: 25: 50) *
- Mezcla 100: Mezcla 1 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 101: Mezcla 57 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 102: Mezcla 91 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 103: Mezcla 3 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 104: Mezcla 94 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 105: Mezcla 2 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 106: Mezcla 97 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 107: Mezcla 29 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 108: $\text{CuHPO}_3 + \text{Fe}_2(\text{HPO}_3)_3 + \text{K}_2\text{HPO}_3$ (34: 33: 33) *
- Mezcla 109: Mezcla 108 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 110: Mezcla 22 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 111: $\text{CuHPO}_3 + \text{Al}_2(\text{HPO}_3)_3 + \text{K}_2\text{HPO}_3$ (34: 33: 33) *
- Mezcla 112: Mezcla 111 + IR5885 (750⁽¹⁾: 15⁽²⁾)

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- Mezcla 113: Mezcla 64 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 114: CuHPO₃ + (NH₄)₂HPO₃ + CaHPO₃ (34: 33: 33) *
- Mezcla 115: Mezcla 114 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 116: CuHPO₃ + (NH₄)₂HPO₃ + ZnHPO₃ (34: 33: 33) *
- Mezcla 117: Mezcla 116 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 118: CuHPO₃ + (NH₄)₂HPO₃ + MnHPO₃ (34: 33: 33) *
- Mezcla 119: Mezcla 118 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 120: CuHPO₃ + (NH₄)₂HPO₃ + Fe₂(HPO)₃ (34:33:33) *
- Mezcla 121: Mezcla 120 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 122: CuHPO₃ + (NH₄)₂HPO₃ + Al₂(HPO₃)₃ (34: 33: 33) *
- Mezcla 123: Mezcla 122 + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 124: CuHPO₃ + IR5885 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 125: CuHPO₃ + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 126: Mezcla 1 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 127: Mezcla 57 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 128: Mezcla 91 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 129: Mezcla 3 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 130: Mezcla 94 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 131: Mezcla 2 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 132: Mezcla 97 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 133: Mezcla 29 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 134: Mezcla 108 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 135: Mezcla 22 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 136: Mezcla 111 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 137: Mezcla 64 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 138: Mezcla 114 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 139: Mezcla 116 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 140: Mezcla 118 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 141: Mezcla 120 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 142: Mezcla 122 + IR6141 (750⁽¹⁾: 15⁽²⁾)
- Mezcla 143: CuHPO₃ + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 144: Mezcla 1 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 145: Mezcla 3 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 146: Mezcla 2 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 147: Mezcla 22 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 148: Mezcla 57 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 149: Mezcla 64 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)

- Mezcla 150: Mezcla 91 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 151: Mezcla 114 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 152: CuHPO₃ + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 153: Mezcla 1 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 154: Mezcla 3 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 155: Mezcla 2 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 156: Mezcla 22 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 157: Mezcla 57 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 158: Mezcla 64 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 159: Mezcla 91 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 160: Mezcla 114 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 161: CuHPO₃ + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 162: Mezcla 1 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 163: Mezcla 2 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 164: Mezcla 3 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 165: Mezcla 22 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 166: Mezcla 57 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 167: Mezcla 64 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 168: Mezcla 91 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 169: Mezcla 114 + Benalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 170: CuHPO₃ + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 171: Mezcla 1 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 172: Mezcla 2 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 173: Mezcla 3 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 174: Mezcla 22 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 175: Mezcla 57 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 176: Mezcla 64 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 177: Mezcla 91 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 178: Mezcla 114 + Metalaxil (750⁽¹⁾: 15⁽²⁾)
- Mezcla 179: CuHPO₃ + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 180: Mezcla 1 + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 181: Mezcla 2 + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 182: Mezcla 3 + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 183: Mezcla 22 + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 184: Mezcla 57 + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 185: Mezcla 64 + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 186: Mezcla 91 + Metalaxil-M (750⁽¹⁾: 15⁽²⁾)

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- Mezcla 187: Mezcla 114+Metalaxil-M (750⁽¹⁾: 15⁽²⁾)
- Mezcla 188: CuHPO₃ + Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 189: Mezcla 1+ Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 190: Mezcla 2+ Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 191: Mezcla 3+ Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 192 Mezcla 22+ Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 193: Mezcla 57+ Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 194: Mezcla 64+ Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 195: Mezcla 91+ Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 196: Mezcla 114+Iprovalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 197: CuHPO₃ + Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 198: Mezcla 1 +Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 199: Mezcla 2 +Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 200: Mezcla 3 +Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 201: Mezcla 22+Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 202: Mezcla 57+Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 203: Mezcla 64+Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 204: Mezcla 91+Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 205: Mezcla 114+Axoxistrobin (750⁽¹⁾: 10⁽²⁾)
- Mezcla 206: CuHPO₃ + Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 207: Mezcla 1+ Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 208: Mezcla 2 + Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 209: Mezcla 3 + Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 210: Mezcla 22 + Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 211: Mezcla 57 + Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 212: Mezcla 64 + Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 213: Mezcla 91 + Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 214: Mezcla 114+ Metominofén (750⁽¹⁾: 10⁽²⁾)
- Mezcla 215: CuHPO₃ + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 216: Mezcla 1 + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 217: Mezcla 2 + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 218: Mezcla 3 + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 219: Mezcla 22 + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 220: Mezcla 57 + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 221: Mezcla 64 + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 222: Mezcla 91 + Acibenzolar (750⁽¹⁾: 20⁽²⁾)
- Mezcla 223: Mezcla 114+ Acibenzolar (750⁽¹⁾: 20⁽²⁾)

- Mezcla 224: CuHPO_3 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 225: Mezcla 1 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 226: Mezcla 2 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 227: Mezcla 3 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 228: Mezcla 22 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 229: Mezcla 57 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 230: Mezcla 64 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 231: Mezcla 91 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 232: Mezcla 114 + Ciazofamida ($750^{(1)}$: $10^{(2)}$)
- Mezcla 233: CuHPO_3 + Clorotalonilo ($750^{(1)}$: $100^{(2)}$)
- Mezcla 234: Mezcla 1 + Clorotalonilo ($750^{(a)}$: $100^{(2)}$)
- Mezcla 235: Mezcla 2 + Clorotalonilo ($750^{(1)}$: $100^{(2)}$)
- Mezcla 236: Mezcla 3 + Clorotalonilo ($750^{(1)}$: $100^{(2)}$)
- Mezcla 237: Mezcla 22 + Clorotalonilo ($750^{(1)}$: $100^{(2)}$)
- Mezcla 238: Mezcla 57 + Clorotalonilo ($750^{(1)}$: $100^{(2)}$)
- Mezcla 239: Mezcla 64 + Clorotalonilo ($750^{(a)}$: $100^{(2)}$)
- Mezcla 240: Mezcla 91 + Clorotalonilo ($750^{(a)}$: $100^{(2)}$)
- Mezcla 241: Mezcla 114 + Clorotalonilo ($750^{(1)}$: $100^{(2)}$)
- Mezcla 242: CuHPO_3 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 243: Mezcla 1 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 244: Mezcla 2 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 245: Mezcla 3 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 246: Mezcla 22 + mezcla de Burdeos ($750^{(a)}$: $200^{(3)}$)
- Mezcla 247: Mezcla 57 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 248: Mezcla 64 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 249: Mezcla 91 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 250: Mezcla 114 + mezcla de Burdeos ($750^{(1)}$: $200^{(3)}$)
- Mezcla 251: CuHPO_3 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 252: Mezcla 1 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 253: Mezcla 2 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 254: Mezcla 3 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 255: Mezcla 22 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 256: Mezcla 57 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 257: Mezcla 64 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 258: Mezcla 91 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 259: Mezcla 114 + $\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $100^{(3)}$)
- Mezcla 260: CuHPO_3 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)

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- Mezcla 261: Mezcla 1 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 262: Mezcla 2 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 263: Mezcla 3 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 264: Mezcla 22 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 265: Mezcla 57 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 266: Mezcla 64 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 267: Mezcla 91 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 268: Mezcla 114 + CuSO_4 ($750^{(1)}$: $100^{(3)}$)
- Mezcla 269: CuHPO_3 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 270: Mezcla 1 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 271: Mezcla 2 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 272: Mezcla 3 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 273: Mezcla 22 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 274: Mezcla 57 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 275: Mezcla 64 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 276: Mezcla 91 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 277: Mezcla 114 + $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ($750^{(1)}$: $200^{(3)}$)
- Mezcla 278: CuHPO_3 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 279: Mezcla 1 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 280: Mezcla 2 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 281: Mezcla 3 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 282: Mezcla 22 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 283: Mezcla 57 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 284: Mezcla 64 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 285: Mezcla 91 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 286: Mezcla 114 + Airone ($750^{(1)}$: $40^{(3)}$)
- Mezcla 287: CuHPO_3 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 288: Mezcla 1 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 289: Mezcla 2 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 290: Mezcla 3 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 291: Mezcla 22 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 292: Mezcla 57 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 293: Mezcla 64 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 294: Mezcla 91 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 295: Mezcla 114 + Piraclostrobin ($750^{(1)}$: $10^{(2)}$)
- Mezcla 296: CuHPO_3 + Bentiavalicarb ($750^{(1)}$: $15^{(2)}$)
- Mezcla 297: Mezcla 1 + Bentiavalicarb ($750^{(1)}$: $15^{(2)}$)

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- Mezcla 298: Mezcla 2 + Bentiavalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 299: Mezcla 3 + Bentiavalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 300: Mezcla 22 + Bentiavalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 301: Mezcla 57 + Bentiavalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 302: Mezcla 64 + Bentiavalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 303: Mezcla 91 + Bentiavalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 304: Mezcla 114 + Bentiavalicarb (750⁽¹⁾: 15⁽²⁾)
- Mezcla 305: CuHPO₃ + Cimoxanilo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 306: Mezcla 1 + Cimoxanilo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 307: Mezcla 2 + Cimoxanilo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 308: Mezcla 3 + Cimoxanilo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 309: CuHPO₃ + Oxadixilo (750⁽¹⁾: 15⁽²⁾)
- Mezcla 310: Mezcla 1 + Oxadixilo (750⁽¹⁾: 15⁽²⁾)
- Mezcla 311: Mezcla 2 + Oxadixilo (750⁽¹⁾: 15⁽²⁾)
- Mezcla 312: Mezcla 3 + Oxadixilo (750⁽¹⁾: 15⁽²⁾)
- Mezcla 313: CuHPO₃ + Ofurace (750⁽¹⁾: 15⁽²⁾)
- Mezcla 314: Mezcla 1 + Ofurace (750⁽¹⁾: 15⁽²⁾)
- Mezcla 315: Mezcla 2 + Ofurace (750⁽¹⁾: 15⁽²⁾)
- Mezcla 316: Mezcla 3 + Ofurace (750⁽¹⁾: 15⁽²⁾)
- Mezcla 317: CuHPO₃ + Famoxadona (750⁽¹⁾: 100⁽²⁾)
- Mezcla 318: Mezcla 1 + Famoxadona (750⁽¹⁾: 100⁽²⁾)
- Mezcla 319: Mezcla 2 + Famoxadona (750⁽¹⁾: 100⁽²⁾)
- Mezcla 320: Mezcla 3 + Famoxadona (750⁽¹⁾: 100⁽²⁾)
- Mezcla 321: CuHPO₃ + Fenamidone (750⁽¹⁾: 50⁽²⁾)
- Mezcla 322: Mezcla 1 + Fenamidone (750⁽¹⁾: 50⁽²⁾)
- Mezcla 323: Mezcla 2 + Fenamidone (750⁽¹⁾: 50⁽²⁾)
- Mezcla 324: Mezcla 3 + Fenamidone (750⁽¹⁾: 50⁽²⁾)
- Mezcla 325: CuHPO₃ + Fluazinam (750⁽¹⁾: 100⁽²⁾)
- Mezcla 326: Mezcla 1 + Fluazinam (750⁽¹⁾: 100⁽²⁾)
- Mezcla 327: Mezcla 2 + Fluazinam (750⁽¹⁾: 100⁽²⁾)
- Mezcla 328: Mezcla 3 + Fluazinam (750⁽¹⁾: 100⁽²⁾)
- Mezcla 329: CuHPO₃ + Dimetomorfo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 330: Mezcla 1 + Dimetomorfo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 331: Mezcla 2 + Dimetomorfo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 332: Mezcla 3 + Dimetomorfo (750⁽¹⁾: 100⁽²⁾)
- Mezcla 333: CuHPO₃ + Mancozeb (750⁽¹⁾: 200⁽²⁾)
- Mezcla 334: Mezcla 1 + Mancozeb (750⁽¹⁾: 200⁽²⁾)

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- Mezcla 335: Mezcla 2 + Mancozeb (750⁽¹⁾: 200⁽²⁾)
- Mezcla 336: Mezcla 3 + Mancozeb (750⁽¹⁾: 200⁽²⁾)
- Mezcla 337: CuHPO₃ + Tolilfluanida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 338: Mezcla 1 + Tolilfluanida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 339: Mezcla 2 + Tolilfluanida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 340: Mezcla 3 + Tolilfluanida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 341: CuHPO₃ + Folpet (750⁽¹⁾: 100⁽²⁾)
- Mezcla 342: Mezcla 1 + Folpet (750⁽¹⁾: 100⁽²⁾)
- Mezcla 343: Mezcla 2 + Folpet (750⁽¹⁾: 100⁽²⁾)
- Mezcla 344: Mezcla 3 + Folpet (750⁽¹⁾: 100⁽²⁾)
- Mezcla 345: CuHPO₃ + Propamocarb (750⁽¹⁾: 200⁽²⁾)
- Mezcla 346: Mezcla 1 + Propamocarb (750⁽¹⁾: 200⁽²⁾)
- Mezcla 347: Mezcla 2 + Propamocarb (750⁽¹⁾: 200⁽²⁾)
- Mezcla 348: Mezcla 3 + Propamocarb (750⁽¹⁾: 200⁽²⁾)
- Mezcla 349: CuHPO₃ + Zoxamida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 350: Mezcla 1 + Zoxamida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 351: Mezcla 2 + Zoxamida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 352: Mezcla 3 + Zoxamida (750⁽¹⁾: 100⁽²⁾)
- Mezcla 353: CuHPO₃ + Syngenta⁽⁴⁾ (750⁽¹⁾: 15⁽²⁾)
- Mezcla 354: Mezcla 1 + Syngenta⁽⁴⁾ (750⁽¹⁾: 15⁽²⁾)
- Mezcla 355: Mezcla 2 + Syngenta⁽⁴⁾ (750⁽¹⁾: 15⁽²⁾)
- Mezcla 356: Mezcla 3 + Syngenta⁽⁴⁾ (750⁽¹⁾: 15⁽²⁾)
- Mezcla 357: CuHPO₃ + Etaboxam (750⁽¹⁾: 50⁽²⁾)
- Mezcla 358: Mezcla 1 + Etaboxam (750⁽¹⁾: 50⁽²⁾)
- Mezcla 359: Mezcla 2 + Etaboxam (750⁽¹⁾: 50⁽²⁾)
- Mezcla 360: Mezcla 3 + Etaboxam (750⁽¹⁾: 50⁽²⁾)
- Mezcla 361: CuHPO₃ + Sacarina (750⁽¹⁾: 125⁽²⁾)
- Mezcla 362: Mezcla 1 + Sacarina (750⁽¹⁾: 125⁽²⁾)
- Mezcla 363: Mezcla 2 + Sacarina (750⁽¹⁾: 125⁽²⁾)
- Mezcla 364: Mezcla 3 + Sacarina (750⁽¹⁾: 125⁽²⁾)

* proporciones recíprocas expresadas en equivalentes de ácido fosforoso.

(1): dosis expresada en ppm de equivalentes de ácido fosforoso.

(2): dosis expresada en ppm del ingrediente activo.

(3): dosis expresada en ppm de equivalentes de cobre metálico.

(4): el compuesto fungicida (32).

Ejemplo 5

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Eficacia de las composiciones fungicidas, objeto de la presente invención, en el control de Plasmopara viticola a las vides en aplicación preventiva al follaje. Tablas 1-2

Se tratan hojas de vides cultivadas de Merlot, sembradas en jarrones, en un ambiente acondicionado (20±1°C, 70% humedad relativa) rociando ambos lados de las hojas con las mezclas en examen dispersadas en una solución acuosa que contiene 0.3% de Tween® 20.

Después de 7 días en ambiente acondicionado, la plantas se infectan por el envés con una suspensión acuosa de esporas de Plasmopara viticola (200.000 esporas por cm³).

La plantas se mantienen en un ambiente de humedad saturada, a 21°C, durante el periodo de incubación del hongo y, al final de este periodo (7 días), se evalúa la actividad fungicida conforme a una escala de evaluación en porcentaje que va de 100 (planta sana) a 0 (planta completamente infectada).

A partir de los datos indicados en las tablas1-2, es posible verificar el efecto sinérgico de las mezclas, compuestas por las mezclas que se están examinando, comparada con la eficacia esperada con el uso de la fórmula de Limpel ("Pesticide Science" (1987), vol. 19, páginas 309-315):

$$E = x + y - (xy/100)$$

en donde:

E es la actividad fungicida esperada, en ausencia de efectos sinérgicos, de una mezcla obtenida mezclando g.x del compuesto X con g.y de el compuesto Y; x es la actividad del compuesto X cuando se usa solo con una dosificación de g.x; y es la actividad del compuesto Y cuando se usa solo con una dosificación de g.y.

Cuando la actividad fungicida que se encuentra de forma experimental es mayor que el valor de E, esta actividad se considera sinérgica.

Tabla 1

Siete días de actividad preventiva sobre Plasmopara viticola, con aplicación sobre las hojas de las vides, de mezclas (50:50)* de sal cúprica (II) del ácido fosforoso (CuHPO₃), las cuales a 500 ppm** (g.x) es 88 (x) con otras sales metálicas del ácido fosforoso.

Mezcla	Dosis ppm** (g.y)	Actividad (y)	Actividad de la mezcla Limpel (E)	Actividad experimental de la mezcla	Factor de sinergismo
CaHPO ₃	500	0	88	100	1,14
ZnHPO ₃	500	25	91	100	1,10
MnHPO ₃	500	0	88	98	1,11
(NH ₄) ₂ HPO ₃	500	38	92,5	98	1,06
K ₂ HPO ₃	500	45	93,4	99	1,06

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* proporciones recíprocas expresadas en equivalentes de ácido fosforoso.
* * las dosis en ppm se refieren a la cantidad de equivalentes de ácido fosforoso.

Tabla 2

Siete días de actividad preventiva sobre Plasmopara viticola, con aplicación sobre las hojas de las vides, de mezclas del compuesto de sacarina (el compuesto No. 34), el cual a 500 ppm (g.x) es 45 (x) con una o más sales metálicas del ácido fosforoso.

Mezcla	Dosis ppm** (g. <u>y</u>)	Actividad (y)	Actividad de la mezcla Limpel (E)	Actividad experimental de la mezcla	Factor de sinergismo
CuHPO ₃	250	35	64,2	100	1,56
CuHPO ₃ + CaHPO ₃ (50:50)*	250	50	72,5	100	1,38
CuHPO ₃ + MnHPO ₃ (50:50)*	250	52	73,6	98	1,33
CuHPO ₃ + MnHPO ₃ (50:50)*	250	47	70,8	95	1,34
CuHPO ₃ + MnHPO ₃ (66:34)*	250	56	75,8	98	1,29

* proporciones recíprocas expresadas en equivalentes de ácido fosforoso.
** las dosis en ppm se refieren a la cantidad de equivalentes de ácido fosforoso.

Ejemplo 6

Eficacia de las composiciones fungicidas, objeto de la presente invención, en el control de la Phytophthora infestans sobre plantas de papa en aplicación preventiva al follaje. Tablas 3-6

Se tratan hojas de plantas de papa, de la variedad Primura, cultivadas en macetas, en un ambiente acondicionado (20 ± 1°C, 70% humedad relativa) rociando ambos lados de las hojas con las mezclas que es van a examinar dispersadas en una solución acuosa que contiene 0.3% de Tween® 20.

Después de permanecer 7 días en un ambiente acondicionado, la plantas se infectan por el envés con una suspensión acuosa de esporas de Phytophthora infestans (100.000 esporas por cm³). La plantas se mantienen en un ambiente de humedad saturada, a 18-24°C, durante el periodo de incubación del hongo y, al final de este periodo (7 días), se evalúa la actividad fungicida conforme a una escala de evaluación en porcentaje que va de 100 (planta sana) a 0 (planta completamente infectada).

A partir de los datos indicados en las tablas3-6, es posible verificar el efecto sinérgico de las mezclas, compuestas por las mezclas que se están examinando, comparadas con la eficacia esperada con el uso de la fórmula de Limpel.

Tabla 3

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Siete días de actividad preventiva sobre *Phytophthora infestans*, con aplicación sobre las hojas de plantas de papa, de mezclas (50:50)* de sal cúprica (II) del ácido fosforoso (CuHPO_3), la cual a 750 ppm** (g.x) es 12 (x) con otras sales metálicas del ácido fosforoso.

Mezcla	Dosis ppm** (g.y)	Actividad (y)	Actividad de la mezcla Limpel (E)	Actividad experimental de la mezcla	Factor de sinergismo
CaHPO_3	750	10	18,8	78	4,1
ZnHPO_3	750	5	16,4	70	4,2
MnHPO_3	750	15	25,2	80	3,2
$(\text{NH}_4)_2\text{HPO}_3$	750	5	16,4	68	4,1
K_2HPO_3	750	5	16,4	65	3,9

* proporciones recíprocas expresadas en equivalentes de ácido fosforoso.

** las dosis en ppm se refieren a la cantidad de equivalentes de ácido fosforoso.

Tabla 4

Siete días de actividad preventiva sobre *Phytophthora infestans*, con aplicación sobre las hojas plantas de papa, de mezclas del compuesto IR5885 (el compuesto No. 1), el cual a 15 ppm (g.x) es 40 (x) con una o más sales metálicas del ácido fosforoso.

Mezcla	Dosis ppm** (g.y)	Actividad (y)	Actividad de la mezcla Limpel (E)	Actividad experimental de la mezcla	Factor de sinergismo
CuHPO_3	750	12	47,2	95	2,01
$\text{CuHPO}_3 + \text{CaHPO}_3$ (50:50)*	750	78	86,8	95	1,09
$\text{CuHPO}_3 + \text{MnHPO}_3$ (50:50)*	750	70	82	90	1,1
$\text{CuHPO}_3 + \text{MnHPO}_3$ (50:50)*	750	80	88	93	1,05
$\text{CuHPO}_3 + \text{MnHPO}_3$ (66:34)*	750	75	78,7	90	1,14

* proporciones recíprocas expresadas en equivalentes de ácido fosforoso.

** las dosis en ppm se refieren a la cantidad de equivalentes de ácido fosforoso.

Tabla 5

Siete días de actividad preventiva sobre *Phytophthora infestans*, con aplicación sobre las hojas plantas de papa, de mezclas de el compuesto IR6141 (el compuesto No. 2), el cual a 50 ppm (g.x) es 35 (x) con una o más sales metálicas del ácido fosforoso.

Mezcla	Dosis ppm** (g.y)	Actividad (y)	Actividad de la mezcla Limpel (E)	Actividad experimental de la mezcla	Factor de sinergismo
CuHPO_3	750	12	42,8	90	2,10
$\text{CuHPO}_3 + \text{CaHPO}_3$ (50:50)*	750	78	85,7	94	1,09

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CuHPO ₃ + MnHPO ₃ (50:50)*	750	70	80,5	93	1,15
CuHPO ₃ + MnHPO ₃ (50:50)*	750	80	87	96	1,10
CuHPO ₃ + MnHPO ₃ (66:34)*	750	75	85	94	1,1

* proporciones recíprocas expresadas en equivalentes de ácido fosforoso.

** las dosis en ppm se refieren a la cantidad de equivalentes de ácido fosforoso.

Tabla 6

Siete días de actividad preventiva sobre Phytophthora infestans, cepa resistente a fenilalanina, con aplicación sobre las hojas plantas de papa, de mezclas del compuesto IR6141 (el compuesto No. 2), el cual a 50 ppm (g.x) es 5 (x) con una o más sales metálicas del ácido fosforoso.

Mezcla	Dosis ppm** (g.y)	Actividad (y)	Actividad de la mezcla Limpel (E)	Actividad experimental de la mezcla	Factor de sinergismo
CuHPO ₃	750	12	16,4	85	5,2
CuHPO ₃ + CaHPO ₃ (50:50)*	750	78	79,1	90	1,14
CuHPO ₃ + MnHPO ₃ (50:50)*	750	70	71,5	88	1,23
CuHPO ₃ + MnHPO ₃ (50:50)*	750	80	81	94	1,16
CuHPO ₃ + MnHPO ₃ (66:34)*	750	77	78,1	90	1,15

* proporciones recíprocas expresadas en equivalentes de ácido fosforoso.

** las dosis en ppm se refieren a la cantidad de equivalentes de ácido fosforoso.

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REIVINDICACIONES 1.

1. Una composición fungicida compuesta por mezclas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso o compuestas por mezclas que comprenden una sal cúprica (II) del ácido fosforoso, sola o mezclada con por lo menos otra sal metálica del ácido fosforoso, y uno o más compuestos fungicidas.
2. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque la sal metálica del ácido fosforoso es una sal de un metal alcalino, un metal alcalinotérreo, una sal de amonio o una sal de Fe, Mn, Zn, Ni, Al, Ti o Se.
3. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque la sal metálica del ácido fosforoso es una sal mono o bibásica, o una mezcla de éstas en cualquier proporción.
4. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque las mezclas también contienen metales alcalinos en porcentajes no mayores de 10% en peso.
5. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque el compuesto fungicida se selecciona de entre:
 - (1) IR5885, un compuesto dipeptídico que corresponde a mezclas diastereoisoméricas de metil[S-(R,S)]-[3-(N-isopropoxycarbonilvalinil)-amino]-3-(4-cloro-fenil) propanoato en cualquier proporción, o a una de las dos formas diastereoisoméricas S-R o S-S tomadas individualmente;
 - (2) IR6141, que corresponde a alaninato de N-(fenilacetil)-N-2,6-xilil-R-metilo;
 - (3) Ácido salicílico (SA) o sus derivados como ácido acetilsalicílico (ASA), sales cúpricas de ácido salicílico o del ácido acetilsalicílico;
 - (4) Una sal cúprica (I) o sal cúprica (II), como oxiclورو de cobre, hidróxido de cobre, mezcla de Burdeos, sulfato de cobre, o una mezcla de hidróxido y oxiclورو de cobre (Airone);
 - (5) Benalaxil que corresponde a alaninato de N-(fenilacetil)-N-2,6-xilil-RS-metilo;
 - (6) Metalaxil que corresponde a alaninato de N-(2-metoxiacetil)-N-2,6-xilil-RS-metilo;
 - (7) Metalaxil-M que corresponde a alaninato de N-(2-metoxiacetil)-N-2,6-xilil-R-metilo;
 - (8) Oxadixilo que corresponde a 2-metoxi-N-(2-oxo-1,3-oxazolidin-3-il)aceto-2',6'-xilidida;



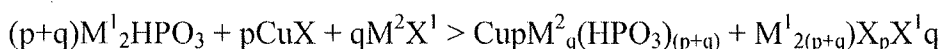
- (9) Ofurace que corresponde a DL-3-[N-cloroacetil-N-(2,6-xilil)-amino]- γ -butirolactona;
- (10) Iprovalicarb que corresponde a O-(1-metil-etil)-N-[2-metil-1-[[[1-(4-metil-fenil)-etil] amino]carbonil]propil]carbamato;
- (11) Bentiavalicarb-isopropilo que corresponde a O-isopropil [(S)-1-{{(1R)-1-(6-fluoro-1,3-benzo-tiazol-2-il)etil]-carbamoil-2-metilpropil]-carbamato;
- (12) Cimoxanilo que corresponde a 1-(2-ciano-2-metoxiimino-acetil)-3-etilurea;
- (13) Azoxistrobin que corresponde a (E)-2-[2-[6-(2-cianofenoxi)-pirimidin-4-ilo]fenil-3-metilmetoxiacrilato];
- (14) Metominofén que corresponde a N-metil-(E)-metoxiimino-(2-fenoxifenil)acetamida;
- (15) Piraclostrobin que corresponde a metil N-(2-[1-(4-clorofenil)pirazol-3-ioximetil]-fenil)-N-metoxicarbamato;
- (16) Acibenzolar-S-metil que corresponde a metil benzo(1,2,3)tiadiazol-7-tiocarboxilato;
- (17) Famoxadona que corresponde a 5-metil-5-(4-fenoxifenil)-3-(fenilamino)oxazolidin-2, 4-diona;
- (18) Fenamidone que corresponde a 4-metil-4-fenil-1-(fenilamino)-2-metiltioimidazolidin-5-ona;
- (19) Ciazofamida, que corresponde a 2-ciano-4-cloro-5-(4-metilfenil)-1-(N,N-dimetilamino-sulfamoil)imidazol;
- (20) Fluazinam que corresponde a 3-cloro-N-(3-cloro-5-trifluorometil-2-piridil)- α - α - α -trifluoro-2,6-dinitro-p-toluidina;
- (21) Dimetomorfo que corresponde a (E, Z)-4-[3-(4-clorofenil)-3-(3,4-dimetoxifenil)-acrilol]morfolina; o Flumorfo (SYP-L190) que corresponde a (E, Z)-4-[3-(4-fluorofenil)-3-(3,4-dimetoxifenil)-acrilol]morfolina;
- (22) Flumetover que corresponde a 2-(3,4-dimetoxifenil)-N-etil- α , α , α -trifluoro-N-metil-p-toluamida;
- (23) Clorotalonilo que corresponde a 1,3-diciano-2,4,5,6-tetraclorobenceno;
- (24) Mancozeb que corresponde a la sal de manganeso y zinc de etileno *bis* (ditiocarbamato) (polímero);
- (25) Tolilfluanida que corresponde a N-dicloro-fluorometiltio-N',N'-dimetil-N-p-tolilsulfamida;
- (26) Folpet que corresponde a N-(triclorometil-tio)ftalimida;
- (27) Etridiazol que corresponde a éter etil-3-triclorometil-1,2,4-tiadiazolílico;
- (28) Himexanol que corresponde a 5-metiliso-oxazol-3-ol;

- (29) Propamocarb que corresponde a propil-(3-dimetilaminopropil)carbamato;
- (30) Ácido R-3-aminobutanoico o ácido RS-3-aminobutanoico;
- (31) Zoxamida, que corresponde a 3,5-dicloro-N-(3-cloro-1-etil-1-metil-2-oxopropil)-p-toluamida;
- (32) 2-(4-clorofenil)-N-[2-(3-metoxi-4-prop-2-iniloxi-fenil) etil]-2-prop-2-iniloxi-acetamida;
- (33) Etaboxam, (RS)-(α-ciano-2-tienil)-4-etil-2(etilamino)-5-tiazolcarboxiamida;
- (34) Sacarina
6. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque la sal cúprica (II) del ácido fosforoso y las otras sales metálicas del ácido fosforoso se encuentran presentes en una proporción que va de 10/90 a 90/10 en equivalentes de ácido fosforoso.
7. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque la sal cúprica (II) del ácido fosforoso y las otras sales metálicas del ácido fosforoso se encuentran presentes en una proporción 50/50 en equivalentes de ácido fosforoso.
8. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque la concentración de sustancias activas, la sal cúprica (II) del ácido fosforoso, las otras sales metálicas del ácido fosforoso o los compuestos fungicidas, varía de 0,1% a 98% en peso, de preferencia de 0,5% a 90% en peso.
9. La composición fungicida conforme a la reivindicación 1, que se caracteriza porque está compuesta por una mezcla seleccionada de entre:
- Mezcla 1: $\text{CuHPO}_3 + \text{CaHPO}_3$ (50:50)
 - Mezcla 2: $\text{CuHPO}_3 + \text{ZnHPO}_3$ (50:50)
 - Mezcla 3: $\text{CuHPO}_3 + \text{MnHPO}_3$ (50:50)
 - Mezcla 4: $\text{CuHPO}_3 + \text{MnHPO}_3$ (66:33)
 - Mezcla 100: Mezcla 1 + IR5885 (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 103: Mezcla 3 + IR5885 (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 105: Mezcla 2 + IR5885 (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 124: $\text{CuHPO}_3 + \text{IR5885}$ (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 125: $\text{CuHPO}_3 + \text{IR6141}$ (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 126: Mezcla 1 + IR6141 (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 129: Mezcla 3 + IR6141 (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 131: Mezcla 2 + IR6141 (750⁽¹⁾: 15⁽²⁾)
 - Mezcla 143: $\text{CuHPO}_3 + \text{Cu(SA)}$ (750⁽¹⁾: 64⁽³⁾)
 - Mezcla 144: Mezcla 1 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
 - Mezcla 145: Mezcla 3 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)

- Mezcla 146: Mezcla 2 + Cu(SA) (750⁽¹⁾: 64⁽³⁾)
- Mezcla 152: CuHPO₃ + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 153: Mezcla 1 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 154: Mezcla 3 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 155: Mezcla 2 + Cu(ASA)₂ (750⁽¹⁾: 64⁽³⁾)
- Mezcla 361: CuHPO₃ + Sacarina (750⁽¹⁾: 125⁽²⁾)
- Mezcla 362: Mezcla 1 + Sacarina (750⁽¹⁾: 125⁽²⁾)
- Mezcla 363: Mezcla 2 + Sacarina (750⁽¹⁾: 125⁽²⁾)
- Mezcla 364: Mezcla 3 + Sacarina (750⁽¹⁾: 125⁽²⁾)

10. La composición fungicida conforme a la reivindicación 9, que se caracteriza porque está compuesta por una mezcla seleccionada de entre la mezcla 1, mezcla 2, mezcla 3 y la mezcla 4.
11. Un proceso para la preparación de una composición conforme a la reivindicación 1, que se caracteriza porque las mezclas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso se obtienen mezclando las sales solas o por precipitación conjunta de las mencionadas sales en la mezcla de reacción.
12. El proceso conforme a la reivindicación 11, que se caracteriza porque la precipitación conjunta de las sales se lleva a efecto comenzando a partir de fosfitos, por ejemplo de sodio o potasio, por el desplazamiento del catión metálico M^I con una mezcla, en solución acuosa, de una sal cúprica (II) y la otra sal metálica deseada, conforme al esquema A:

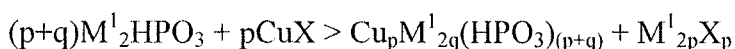
Esquema A



en donde M^I representa un átomo de sodio o potasio, X representa un halógeno, como cloro, bromo, yodo o un grupo sulfato, X^I tiene el mismo significado que X, M² representa un metal alcalinotérreo, un grupo amonio o un átomo de Fe, Mn, Zn, Ni, Al, Ti, Se; p es un número mayor de 0 y menor de 100 y q es igual a 100-p.

13. El proceso conforme a la reivindicación 11, que se caracteriza porque la precipitación conjunta de una sal cúprica (II) del ácido fosforoso y una sal de un metal alcalino del ácido fosforoso se lleva a efecto comenzando a partir de la anterior sal alcalina del ácido fosforoso por desplazamiento parcial del catión metálico con una sal cúprica apropiada (II) conforme al esquema B:

Esquema B



en donde M^I, X, p y q tienen los significados arriba indicados.

14. El proceso conforme a la reivindicación 11, que se caracteriza porque la sustancia activa, es decir, la sal cúprica (II) del ácido fosforoso, otras sales metálicas del ácido fosforoso o los compuestos fungicidas, se diluyen o disuelven en un medio solvente o en un diluyente sólido, posiblemente en presencia de agentes surfactantes.
15. El uso del compuesto fungicida que consta de mezclas que comprenden una sal cúprica (II) del ácido fosforoso y por lo menos otra sal metálica del ácido fosforoso o mezclas que comprenden una sal cúprica (II) del ácido fosforoso, sola o mezclada con por lo menos otra sal metálica del ácido fosforoso, y uno o más compuestos fungicidas, para el control de los hongos fitopatógenos.
16. El uso conforme a la reivindicación 15, que se caracteriza porque los fitopatógenos son: *Plasmopara viticola* (vides); *Phytophthora infestans* (tomate, papa); *Phytophthora nicotianae* (tabaco, plantas ornamentales); *Phytophthora palmivora* (cacao); *Phytophthora cinnamomi* (piña, cítricos); *Phytophthora capsici* (pimiento, tomate, cucurbitáceas); *Phytophthora cryptogea* (tomate, ciruela, plantas ornamentales); *Phytophthora megasperma* (plantas ornamentales); *Phytophthora citri* (cítricos); *Peronospora tabacina* (tabaco); *Pseudoperonospora cubensis* (coliflor, cucurbitáceas); *Pseudoperonospora umili* (lúpulo); *Phytophthora cactorum* (frutales); *Phytophthora destructor* (cebolla); *Phytophthora fragariae* (fresa); *Bremia* (hortaliza).
17. Un método para el control de hongos fitopatógenos en agricultura mediante la aplicación de una composición fungicida conforme a una de las reivindicaciones 1-10.
18. El método conforme a la reivindicación 17, que se caracteriza porque la composición fungicida tiene las siguientes dosificaciones de aplicación por hectárea:
- 1,000-4,000 g de sal del ácido fosforoso;
 - 5-3,500 g para cada compuesto fungicida de (1) a (34) presente en la composición.
19. El método conforme a la reivindicación 17, que se caracteriza porque la aplicación se lleva a cabo en todas las partes de la planta, por ejemplo sobre las hojas, tallos, ramas y raíces, o sobre las semillas mismas antes de sembrar, o sobre la tierra en la cual crece la planta.
20. El método conforme a la reivindicación 17, que se caracteriza porque la aplicación se lleva a efecto para tratamientos preventivos, protectores, profilácticos, sistémicos, curativos o desarraigantes.



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Industria y Comercio
SUPERINTENDENCIA

**REQUISITOS MINIMOS PARA ADMISION A TRAMITE
PCT**

PATENTE DE INVENCION

[☒]

MODELO DE UTILIDAD

[]

- ◆ Indicación de que se solicita la concesión de una patente [☒]
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud [☒]
- ◆ Descripción de la invención [☒]
- ◆ Dibujos de ser estos pertinentes [☒]
- ◆ Comprobante de pago de las tasas establecidas [☒]

COMPLETA [☒]

INCOMPLETA []

DISEÑO INDUSTRIAL []

- ◆ Indicación de que se solicita el registro de Diseño Industrial []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

ESQUEMA DE TRAZADO []

- ◆ Indicación de que se solicita el registro de un Esquema de Trazado []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica del esquema trazado []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

Firma Responsable

Fecha _____

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