



No. 06-095708- -00002-0000

Fecha: 2007-09-19 16:13:07 Dep. 2020 NUECREACIONE
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 467 SOLICIPRORROGA Folios: 2

L- 5381

123

43

Señora

Alix Carmenza Céspedes de Vergel

Jefe de División de Nuevas Creaciones

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

E. _____ S. _____ D. _____

Referencia: Expediente No. 06.095.708

Solicitud de Patente de Invención titulada: "Composición fungicida que
comprende un derivado de ácido fosforoso y tolilfluanida o diclofluanida"

Solicitante: Bayer CropScience S.A.

SOLICITUD DE EXAMEN DE PATENTABILIDAD SEGÚN EL ARTÍCULO 44 DE LA DECISIÓN**486. GACETA NO. 574**

ÁLVARO CORREA ORDÓÑEZ, mayor de edad y vecino de Bogotá D.C., identificado según aparece al pie de mi firma, en mi condición de apoderado de la sociedad arriba mencionada, solicito que se examine la invención de la referencia según los requisitos de patentabilidad previstos en la Decisión 486 de la Comisión de la Comunidad Andina de Naciones. Adjunto recibo de caja por valor de \$404.000 para cubrir la tasa correspondiente según la Resolución 36155 del 28 de diciembre de 2006.

Atentamente,


ÁLVARO CORREA ORDÓÑEZ

C.C.No.79.143.366 de Usaquén

T.P.20.281

Anexo: Recibo de caja No. 07-70990 por valor de \$404.000

44 HX

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-095708- -00002-0000

Fecha: 2007-09-19 16:13:07 Dep. 2020 NUECREACIONE
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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 07 - 70,990
FECHA : SEPTIEMBRE 3 DE 2007

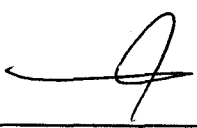
***** CONSIGNACION *****

SITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
RAISBECK LARA RODRIGUEZ	CONSIGNACION	BANCO POPULAR	050-00110-6	48716295	03/09/2007	51,639,850.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	404,000.00
TOTAL :			\$ 404,000.00

SON: CUATROCIENTOS CUATRO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 06-95708

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **574** DE

FECHA **30 DE MARZO DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA LEY

EXPIRA EL **03 DE JULIO DE 2007**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X

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3,341,403

METHOD OF CONTROLLING FUNGI WITH N-THIO - MONOFLUORO - DICHLORO - METHYL IMIDES

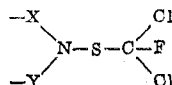
Erich Klauke, Cologne-Flittard, Engelbert Kuhle and Ferdinand Grewe, Cologne-Stammheim, and Helmut Kaspers and Richard Wegler, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

No Drawing. Original application Oct. 31, 1961, Ser. No. 148,845, now Patent No. 3,285,929, dated Nov. 15, 1966. Divided and this application May 31, 1966, Ser. No. 553,663

Claims priority, application Germany, Nov. 3, 1960, F 32,468; Nov. 25, 1960, F 32,620
12 Claims. (Cl. 167-30)

This application is a divisional application of Ser. No. 148,845, filed Oct 31, 1961, now U.S. Pat. No. 3,285,929.

The present invention relates to new and useful improvements in fungicidal preparations and more particularly to improved fungicides. This invention also relates to methods of protecting organic material subject to attack by low orders of organisms. This invention further relates to the synthesis of new chemical compounds, namely N-thiomonofluoro-dichloromethyl imides of the following general formula



in which X stands for organic acyl radicals and Y stands for another acyl radical or another suitable organic radical; X and Y may be linked together, too, to form a common ring system.

Similar compounds of the aforementioned type which contain instead of an =NSCFCl₂-group the



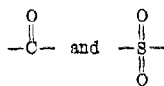
are known already from the literature. U.S. Patents 2,553,770, 2,553,771, 2,553,772, 2,553,773, 2,553,774, 2,553,775, 2,553,776, 2,844,628, for instance, describe a large number of such compounds containing a trichloromethyl-mercapto group.

In accordance with the present invention it has now been found that a large number of organic compounds containing the =NSCFCl₂-group are extremely effective for controlling the growth of fungi, and in this respect are superior to those compounds of the prior art containing the =NSCCl₂-group.

The physiologically active compounds of this invention may thus best be represented as having the



in which the nitrogen is linked to two carbon atoms, two acyl groups or one acyl group and one carbon atom. The phrase acyl group refers especially to the groups of the following character



etc. (see Hackh, "Chemical Dictionary," second edition, page 21). When the nitrogen atom of the



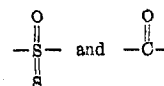
is linked to one acyl group, the compounds may be regarded as amide derivatives. When both of the free linkages of the =NSCFCl₂-group are taken up by acyl groups, the compounds may be regarded as imides (see Sidgwick's "Organic Chemistry of Nitrogen," 1937 edition, pages 136 and 152).

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Suitable amide compounds of the indicated type are thus illustrated in Formula I:

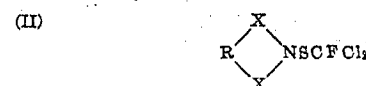


in which R represents an organic residue, possibly linked to X via nitrogen, oxygen or sulfur, too, X is part of an acyl group, such as for example

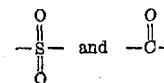


and R' represents an organic radical or a hydrogen radical.

Suitable imide compounds of the indicated type are illustrated by Formula II:

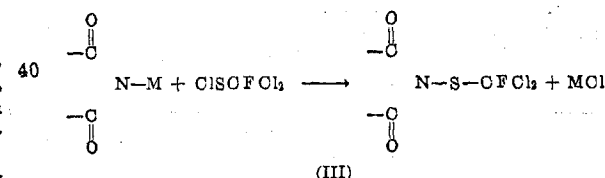


in which R represents one or more organic residues and X is part of an acyl group, such as for example



The organic residue may be aliphatic, aromatic, alicyclic, heterocyclic, and their substituted derivatives, and may be attached furthermore to the above said group also by heteroatoms such as nitrogen, sulfur or oxygen.

The novel compounds of this invention may be prepared in general by the reaction of dichloro-monofluoromethyl-sulphenylchloride (ClSCFCl₂), with the corresponding imide or the metal salt of this compound. Formula III generally illustrates this reaction where M represents hydrogen or a metal, and where both of the acyl groups are derived from carboxylic acid groups:



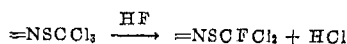
This reaction is shown only to illustrate this invention and not intended to limit it in any way. Other inventive compounds as it may be seen from the examples can be prepared by exactly the same method.

The reaction to prepare the inventive compounds may be carried out at room temperature or at slightly elevated temperature either in an aqueous medium or also in inert organic solvents such as benzene, dioxane, carbon tetrachloride and the like. If the free imides are used, i.e. if M stands for hydrogen, the reaction is carried out with preferably in the presence of acid-binding agents, such as alkali metal hydroxides, -carbonates, -alcoholates, and the like, or also in the presence of tertiary organic amines.

Starting materials for the inventive reaction broadly may be seen from the patent specifications mentioned at the beginning. As some examples of the specifications there may be mentioned: phthalimide, tetrahydrophthalimide, 3,6-endomethylene-Δ⁴-tetrahydrophthalimide, 3-nitrophthalimide, succinic imide, 2,4-dioxothiazolidine, parabanic acid, 1,4-dioxaphthalazine, benzene sulfonic acid methylamide, 4-chlorobenzene-sulfonic acid anilide, chloromethane sulfonic acid anilide or N.N.N'-trimethylsulfamide.

Another method suitable for the preparation of the inventive compounds consists in reacting the thio-trichloromethylamides known from the aforementioned specifications, with anhydrous hydrogen fluoride. Most surprisingly

under even severe reaction conditions only one chlorine atom is split off and replaced by fluorine. The following reaction scheme may illustrate this method:



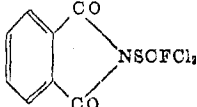
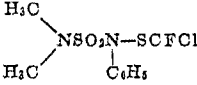
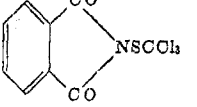
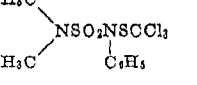
The two bonds before the nitrogen atom may preferably stand for the radical mentioned in the foregoing description.

Anhydrous hydrogen fluoride in the meaning of the above said statement should be a commercial product with a content of about 2% of water, but preferably not more.

The reaction usually is carried out under commercial pressure and at temperatures between 0 and 20° C.; preferably anhydrous hydrogen fluoride is used in an excess so that it serves at the same time as a diluent does. The excess easily can be removed then by distillation. Of course, also other inert solvents may be used as diluents. These inert solvents preferably are nitrobenzene, diethyl-ether, dioxane and the like.

The new inventive compounds as stated above are valuable pesticides with especially fungicidal action and should be used in the field of plant protection. The main advantage of the inventive compounds over the trichloro compounds of the prior art is their better tolerableness on plants especially regarding phytotoxicity, without decreasing in fungicidal activity. A further advantage over the prior art compounds is a longer lasting activity and better stability.

From the following experiment there is to be seen the high initial activity of the inventive compounds. The test is a green-house experiment and has been carried out with tomato plants (Bonny Best). Aqueous emulsions of the compounds shown in the table below have been sprayed on the plants. The aqueous emulsions have been prepared by admixing the active ingredient with the same amount of dimethyl formamide and a commercial non-ionic emulsifier (NP10). Plants sprayed with these solutions are inoculated after 24 hours with zoospores of *Phytophthora infestans*, and placed in humidity chambers at a temperature of 20° C. and a relative humidity of 100%. They are kept there for 5 days. After that the infestation has been checked and is shown in the table below in comparison to an untreated control test, infestation of which is set as 100.

	Degree of infestation at a conc. of active ingredient in percent (aqueous emulsion)	
	0.025	0.0062
	0	5
	0	3
	3	14
	1	13
Control		100

EXAMPLE 1

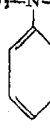
18.5 grams of the potassium salt of phthalimide are dissolved in 100 ml. of toluene and treated with a solu-

tion of 17.0 grams of dichlorofluoromethane sulfenic acid chloride in 50 ml. of toluene at room temperature. Thereby the temperature rises to about 40° C. Heating is continued for about half an hour at 80° C., the reaction mixture then is filtered off the potassium chloride. The crystal obtained is filtered off with suction. After recrystallization from alcohol there are obtained 9 grams of N-dichlorofluoro-methylthiophthalimide of M.P. 152-152.5° C.

EXAMPLE 2

20 grams of N,N-dimethyl-N'-phenylsulfamide and 17 grams of dichlorofluoro-methane sulfenic chloride are dissolved in 100 ml. of toluene and treated with 11 grams of triethylamine at room temperature. Thereby the temperature rises to about 40° C. After stirring for some time water is added, the toluene layer is dried over sodium sulfate and concentrated in vacuum. The crystalline residue melts after recrystallization from alcohol at 110-112° C. There are obtained 18 grams of the N,N-dimethyl-N'-phenyl-N'-dichlorofluoromethyl-thiosulfamide.

In analogous manner there may be obtained the compounds of the following formulae:

$(H_3C)_2N-SO_2-N-SCFCl_2$ 	M.P. 81-82° C.
$(H_3C)_2N-SO_2-N-SCFCl_2$ 	M.P. 97° C.
$(H_3C)_2N-SO_2-N-SCFCl_2$ 	M.P. 60-61° C.
$(H_3C)_2N-SO_2-N-SCFCl_2$ 	M.P. 82° C.
$(H_3C)_2N-SO_2-N-SCFCl_2$ 	M.P. 118° C.

EXAMPLE 3

38 grams of Δ⁴-tetrahydrophthalimide together with 10 grams of caustic soda are dissolved in 170 ml. of water and treated with 43 grams of dichlorofluoromethane-sulfenic acid chloride at a temperature of 13-15° C. The crystal mass obtained is after stirring for some time filtered off with suction and washed with water. The N-dichlorofluoromethyl-thio-tetrahydrophthalimide melts at 102-104° C.

In analogous manner there are obtained the compounds of the following formulae:

	M.P. 46-48° C.
	M.P. 82-84° C.
	M.P. 126-128° C.
	B.P. 141-143° C.

EXAMPLE 4

46.6 grams of benzene sulfanilide together with 8 grams of caustic soda are dissolved in 150 ml. of water and are treated dropwise with 34 grams of dichlorofluoromethane-sulfenic acid chloride at 15-20° C.; the separated crystals are filtered off with suction and the N-thiodichlorofluoromethyl-N-phenyl-benzene-sulfonic acid amide is crystallized from methanol; M.P. 116-120° C.

	M.P. 119° C.
	M.P. 95° C.

EXAMPLE 5

Into a suspension of 5 grams of the potassium salt of phthalimide in 100 ml. of dioxane there are added dropwise 5 grams of fluorodichloro-methane-sulfenic bromide (B.P.₁₁ 24-27° C.), whereby the temperature of the mixture rises to about 30° C. After the addition of water there are obtained 5 grams of N-(dichloro-fluoro-methylthio)-phthalimide of M.P. 152° C.

EXAMPLE 6

37 grams of furfurylidene-benzene-sulfonyl-hydrazon together with 6 grams of sodium hydroxide are dissolved in 200 ml. of water and this solution is treated with 26 grams of fluoro-dichloro-methane sulfenic acid chloride at 15 to 20° C. Thereby crystallization of the mixture occurs. The reaction mixture is stirred for some time and the crystals are then filtered off with suction, M.P. 100-103° C. Yield: 45 grams.

In analogous manner there are obtained the compounds of the following formulae:

	M.P. 87-91° C.
	M.P. 121-123° C.

In an analogous manner there are obtained the compounds of the following formulae:

	M.P. (oil).
	M.P. 52° C.
	M.P. 58° C.
	M.P. 119° C.
	M.P. 136° C.

EXAMPLE 7

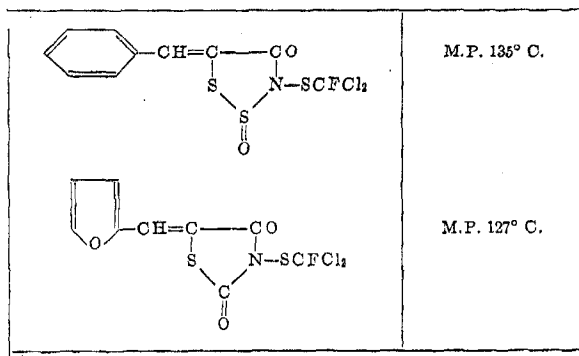
A solution of 26.8 grams of the cyclic sodium salt of maleic acid hydrazide in 200 ml. of water is treated dropwise with 34 grams of fluoro-dichloro-methane sulfenic acid chloride, at a temperature of 10 to 12° C. Thereby a crystal mass is obtained, which after stirring the mixture for some time is filtered off with suction. There are obtained 37 grams of the corresponding sulfenic acid derivative of M.P. 205-210° C. (under decomposition).

EXAMPLE 8

A mixture of 11.7 grams of thiazoline-1,3-dione-(2,4) and 4 grams of sodium hydroxide is dissolved in 100 ml. of water and this solution is treated with 17 grams of fluoro-dichloro-methane-sulfenic acid chloride at a temperature of 10 to 15° C. The separating crystal (21 grams) is filtered off with suction and dried; M.P. 49 to 52° C.

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In analogous manner there are obtained the compounds of the following formulae:



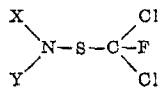
EXAMPLE 9

In to a reaction container, of copper or of stainless steel and provided with a stirrer, a reflux condenser and a thermometer, there are placed 15 grams of N-trichloromethyl-thiophthalimide. Under anhydrous conditions there are added to this solution about 100 grams of anhydrous hydrofluoric acid at a temperature of about 0° C. This mixture is now after stirred for 65 hours while the temperature rises slowly. During the reaction the reflux condenser is cooled with NaCl-ice water and protected against air-humidity with a CaCl₂-tube. The mixture afterwards is poured on 400 grams of ice and the separated residue is filtered off with suction. After washing thoroughly with water there are obtained 13.5 grams of N-dichloro-fluoromethyl-thiophthalimide of M.P. 150–151° C. (from alcohol).

Analysis.—C₉H₄Cl₂FNO₂S.—Calculated: F, 6.78%. Found: F, 6.60%.

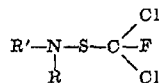
We claim:

1. A method of controlling fungi which comprises contacting fungi with a fungicidally effective amount of a compound having the formula



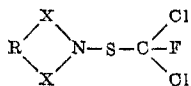
wherein X and Y individually are selected from the group consisting of an organic acyl radical, an aliphatic radical, an aromatic radical and a heterocyclic radical and when X and Y are taken together with the nitrogen atom, a heterocyclic radical, at least one member of X and Y being an organic acyl radical linked to the nitrogen atom through the acyl portion.

2. A method according to claim 1 wherein the compound has the formula



wherein R is selected from the group consisting of an aliphatic radical, an aromatic radical and a heterocyclic radical and R' is an organic acyl radical linked to the nitrogen through the acyl portion.

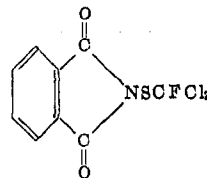
3. A method according to claim 1 wherein the compound has the formula



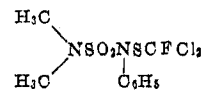
wherein X is an acyl radical and R is selected from the group consisting of an aliphatic, an aromatic and a heterocyclic radical.

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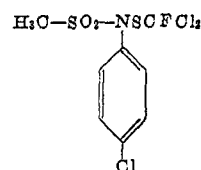
4. A method according to claim 1 wherein the compound has the formula



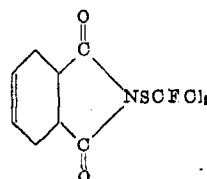
5. A method according to claim 1 wherein the compound has the formula



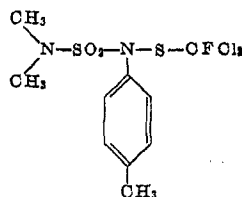
6. A method according to claim 1 wherein the compound has the formula



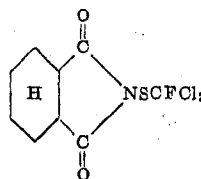
7. A method according to claim 1 wherein the compound has the formula



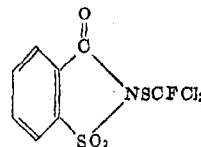
8. A method according to claim 1 wherein the compound has the formula



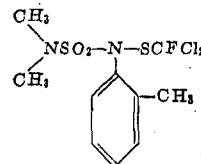
9. A method according to claim 1 wherein the compound has the formula



10. A method according to claim 1 wherein the compound has the formula



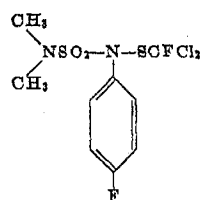
11. A method according to claim 1 wherein the compound has the formula



3,341,403

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12. A method according to claim 1 wherein the compound has the formula



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References Cited

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2,553,771 5/1951 Kittleson ----- 260—326

ALBERT T. MEYERS, *Primary Examiner.*

DALE R. MAHANAND, *Assistant Examiner.*

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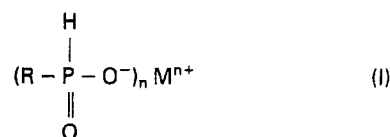
(12) **UK Patent Application** (19) **GB** (11) **2 131 296 A**

- (21) Application No **8332801**
(22) Date of filing **8 Dec 1983**
(30) Priority data
(31) **8220995**
(32) **10 Dec 1982**
(33) **France (FR)**
(43) Application published
20 Jun 1984
(51) **INT CL³**
A01N 57/18 47/34 57/12
59/26
(52) Domestic classification
A5E 217 238 241 248 274
BB
U1S 1275 1306 A5E
(56) Documents cited
None
(58) Field of search
A5E
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(54) **Fungicidal compositions**

(57) Fungicidal compositions comprising, as active ingredient a synergistic mixture of:-

A) - at least one fungicide of the phosphite type of the general formula:



wherein R = OH, alkyl (C₂-C₄) or alkoxy (C₂-C₄), M = H (if R = OH), an alkali metal, an alkaline earth metal or aluminium, and R may also be ONa when M = Na; and n = 1 to 3, and

B) - cymoxanil, are described. ✓

These compositions can be used to protect plants against fungal diseases, in a preventive or curative treatment.

GB 2 131 296 A

SPECIFICATION

Fungicidal compositions

- 5 The present invention relates to new compositions for protecting plants against fungal diseases, and in particular to compositions comprising, as active ingredients, a fungicide of the phosphite type and 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea. 5

It is known to use systemic fungicides to protect plants against fungal diseases. In particular, phosethyl-Al (the common name for aluminium tris-O-ethyl-phosphite or aluminium ethyl-phosphate) is used for protecting vines and other plants against Phycomycetes. This product has a remarkable action in preventive treatment and a secondary curative activity at its normal use dose. It is usually employed in a mixture with contact fungicides. 10

The fungicide 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea (hereinafter referred to as "cymoxanil" which has a limited systemic action and a secondary curative action, is also used. This product is generally used against Phycomycetes in a mixture with a contact fungicide in order to improve its persistence. 15

It has now been found, surprisingly, that if phosethyl-Al or its homologous derivatives as hereinafter defined are used in combination with cymoxanil, the mixtures have a remarkable synergistic action, especially curative action, against fungal diseases.

The present invention accordingly provides fungicidal compositions which comprise, as active ingredient, a mixture of 20

-A) at least one fungicide of the phosphite type of the general formula:



wherein R is an OH group, an alkyl group containing from 2 to 4 carbon atoms or an alkoxy group containing from 2 to 4 carbon atoms, M is a hydrogen atom (only if R is itself an OH group) or an alkali metal, alkaline earth metal or aluminium atom, and R may also represent ONa when M is a sodium atom; and n is an integer from 1 to 3, and 30

-B) 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea.

Amongst the compounds of the general formula I, monosodium and disodium phosphites, and more especially aluminium tris-O-ethyl-phosphonate, are preferred. The weight ratio of B/A is advantageously between 1/100 and 20/100 and preferably between 2/100 and 10/100. The compositions according to the invention can also comprise other active ingredients, for example from one to three contact fungicides chosen from the group consisting of antimildew compounds such as fungicides based on copper, maneb, zineb and zinc metiram (complex of zineb and polyethylenethiuram disulphide), and more especially folpet, captafol and mancozeb or fungicides which are active against other diseases such as botrytis and black rot. 40

The mixtures according to the invention can be prepared as a ready-to-use formulation or can be mixed for immediate use.

The following non-limitative example illustrates the invention and shows how it can be put into practice.

45 Example 45

A mixture of phosethyl-Al (A') and cymoxanil (B) in a weight ratio of B/A' = 6/100 is prepared.

The mixture formulated in this way is used *in vivo* against *Plasmopara viticola* on vine plants in a greenhouse (curative treatment).

Vine plants (Chardonay variety), cultivated in pots, are treated on both sides of their leaves by spraying with an aqueous suspension, at the desired dilution, containing active ingredients to be tested, respectively phosethyl-Al by itself, in the form of a wettable powder containing 80% by weight of active ingredient, cymoxanil by itself, in the form of a ready-to-use wettable powder containing 50% by weight of active ingredient, and a mixture of both wettable powders. 50

The suspension formed in this way is diluted with water, respectively one-fold and two-fold, to give three spraying emulsions having the desired concentration of active ingredients to be tested. Spraying is carried out under conditions such that the spraying of a suspension having a concentration of 1 g/litre corresponds to the application of about 2 microgrammes of active ingredients per cm² of area of plant leaf. 55

In each case, two suspensions each containing one of the active ingredients A' and B at the concentration at which they are present in the mixture are prepared in the same way.

A few days (n = 1 to 3 days) before spraying the active ingredients, the plants were contaminated by spraying the underside of the leaves with an aqueous suspension containing about 80,000 units/cc of spores of *Plasmopara viticola*, which is responsible for vine mildew. The pots were then placed in an incubation cell for 48 hours at 100% relative humidity and at 20°C. 60

The plants are checked 9 days after contamination. The check is made by measuring the sporulated areas

The results are recorded in the table which follows:

5	Product	Dose g/l	Curative Efficacy With Treatment n Day(s) After Contamination			5
			1	2	3	
10	Phosethyl-Al (A')	0.5	0	0	0	10
		1	0	0	0	
		2	70	35	0	
15	Cymoxanil (B)	0.03	15	15	0	15
		0.06	75	75	0	
		0.12	100	80	25	
20	Phosethyl-Al (A') + Cymoxanil (B)	0.5				20
		+0.03	90	75	75	
		1				
		+0.06	97	95	85	
		2				
		+0.12	100	97	85	

25 This table clearly shows that the curative activity of the mixtures at three different doses is superior or very superior to the sum of the activities of phosethyl-Al and cymoxanil taken separately. The protection obtained is still virtually total after 2 days and still good after 3 days, the constituents being inactive in the latter case when they are used separately.

30 This example shows the excellent fungicidal activity of the compositions according to the invention which can be used on various families of phytopathogenic fungi, such as e.g. Phycomycetes, in a preventive or curative treatment.

35 For their use in practice, the compounds according to the invention are not generally employed by themselves. Most frequently, they are used in compositions which comprise, in addition to the active ingredient, an inert carrier (or diluent) and/or a surface-active agent which are compatible with the active ingredient.

These compositions also form part of the present invention. They usually contain from 0.001 to 95% by weight of active ingredient. They generally contain between 0.1% and 20% by weight of surface-active agent.

40 In the present account, the term "carrier" denotes an organic or inorganic, natural or synthetic material with which the active ingredient is combined in order to facilitate its application to the plant, to seeds or to the soil. This carrier is therefore generally inert and it must be acceptable in agriculture, in particular on the plant treated. The carrier can be solid (e.g. clays, natural or synthetic silicates, silica chalks, resins, waxes and solid fertilisers) or liquid (e.g. water, alcohols, ketones, petroleum fractions, aromatic or paraffinic hydrocarbons, chlorohydrocarbons and liquefied gases).

45 The surface-active agent can be an emulsifying, dispersing or wetting agent of ionic or non-ionic type. Examples which may be mentioned are polyacrylic acid salts, lignosulphonic acid salts, phenolsulphonic or naphthalenesulphonic acid salts, polycondensates of ethylene oxide with fatty alcohols, fatty acids, fatty amines or substituted phenols (in particular alkylphenols, arylphenols or styrylphenol), salts of sulphosuccinic acid esters, taurine derivatives (in particular alkyltaurates) and phosphoric acid esters of condensates of ethylene oxide with alcohols or phenols. The presence of at least one surface-active agent is generally essential, especially if the inert carrier is not soluble in water and if the vehicle of application is water.

50 The compositions used in the invention can be in a fairly wide variety of solid or liquid forms. As forms of solid compositions there may be mentioned dusting powders or sprinkling powders (with an active ingredient content which can range up to 100%) and granules.

55 As forms of liquid compositions or compositions which are to be made up into liquid compositions on application, there may be mentioned solutions, in particular water-soluble concentrates, emulsifiable concentrates; emulsions, suspension concentrates, aerosols, wettable powders (or spraying powders) and pastes.

60 The emulsifiable or water-soluble concentrates most frequently comprise 10 to 80% by weight of active ingredient, and the emulsions or solutions which are ready for application contain 0.001 to 20% by weight of active ingredient. In addition to the solvent, and where necessary, the emulsifiable concentrates can contain 2 to 20% by weight of suitable additives such as stabilisers, surface-active agents, penetrating agents, corrosion inhibitors, dyestuffs and adhesives. Starting from these concentrates, emulsions of any desired concentration, which are particularly suitable for application to the leaves, can be obtained by dilution with water.

fluid product which does not form a deposit, and they usually contain from 10 to 75% by weight of active ingredient, from 0.5 to 15% by weight of surface-active agents, from 0.1 to 10% by weight of thixotropic agent, from 0 to 10% by weight of suitable additives such as anti-foam agents, corrosion inhibitors, stabilisers, penetrating agents and adhesives, and, as the carrier, water or an organic liquid in which the active ingredient is sparingly soluble or insoluble; certain organic solids, or inorganic salts, can be dissolved in the carrier in order to assist in preventing sedimentation or to act as anti-freeze agents for the water.

The wettable powders (or spraying powders) are usually prepared so as to contain 20 to 95% by weight of active ingredient, and they usually contain, in addition to the solid carrier, from 0 to 5% by weight of a wetting agent, from 3 to 10% by weight of a dispersing agent and, where necessary, from 0 to 10% by weight of one or more stabilisers and/or other additives such as penetrating agents, adhesives, anti-caking agents and dyestuffs.

Various compositions of wettable powders are now given as examples:

Example 2

15	- active ingredients (6.5/100 mixture of B/A)	50 %	15
	- ethylene oxide/fatty alcohol condensate (wetting agent)	2.5%	
20	- ethylene oxide/styrylphenol condensate (dispersing agent)	5 %	20
	- chalk (inert carrier)	42.5%	
25			25

Another example of wettable powder has the following composition:

Example 3

30	- active ingredient (6.6/100 mixture of B/A')		30
	✓ phosethyl-AL	50 %	
	cymoxanil	3.3%	
35	✓ folpet	25 %	35
	- ethylene oxide/fatty alcohol condensate (wetting agent)	5.7%	
40	- ethylene oxide/styrylphenol condensate (dispersing agent)	6 %	40

To obtain these spraying powders or wettable powders, the active ingredient is intimately mixed with the additional substances in suitable mixers and the mixture is ground in mills or other suitable grinders. This gives spraying powders of advantageous wettability and suspendability; they can be suspended in water at any desired concentration and this suspension can be used very advantageously, in particular for application to the leaves of the plants.

As already stated, the aqueous dispersions and aqueous emulsions, e.g. compositions obtained by diluting, with water, a wettable powder or an emulsifiable concentrate according to the invention, are included within the general scope of the present invention. The emulsions can be of the water-in-oil or oil-in-water type and they can have a thick consistency such as that of a "mayonnaise".

The granules, which are intended to be placed on the soil, are usually prepared so as to have dimensions of between 0.1 to 2 mm, and they can be manufactured by agglomeration or impregnation. In general, the granules contain 0.5 to 25% by weight of active ingredient and 0 to 10% by weight of additives such as stabilisers, slow release modifiers, binders and solvents.

Compositions according to the present invention may also be in the form of dusting powders; thus, it is possible to use a composition comprising 50 g of active ingredient and 950 g of talc; it is also possible to use a composition comprising 20 g of active ingredient, 10 g of finely divided silica and 970 g of talc; these constituents are mixed and ground and the mixture is applied by dusting.

The invention also relates to a method for treating plants against attack by phytopathogenic fungi which comprises applying to these plants an effective amount of a mixture of A) at least one compound of general formula I (wherein R, M and n are as hereinbefore defined) and B) 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea in a composition according to the present invention, for example after contamination of the plants

the fungi present on these plants to be controlled and destroyed. However, the use doses can vary within wide limits, according to the fungus to be combated, the type of crop and the climatic conditions.

CLAIMS

- 5 1. Fungicidal compositions which comprise, as active ingredient a mixture of:-
-A) at least one fungicide of the phosphite type of the general formula:-



- 15 wherein R is an OH group, an alkyl group containing from 2 to 4 carbon atoms or an alkoxy group containing from 2 to 4 carbon atoms, M is a hydrogen atom (only if R is itself an OH group) or an alkali metal, alkaline earth metal or aluminium atom, and R may also represent ONa when M is a sodium atom; and n is an integer from 1 to 3, and -B) 1-(2-cyano-2-methoxyiminoacetyl)-3-ethylurea, and optionally an inert carrier and/or surface active agent which is compatible with the active ingredient.
- 20 2. Compositions according to claim 1, wherein the weight ratio of B/A is between 1/100 and 20/100.
3. Compositions according to claim 1 wherein the weight ratio of B/A is between 2/100 and 10/100.
4. Compositions according to any one of claims 1 to 3, wherein the compound A is aluminium tris-O-ethyl-phosphonate.
- 25 5. Compositions according to any one of claims 1 to 4, which also comprise, as active ingredient, from one to three contact fungicides.
6. Compositions according to any one of claims 1 to 4 which also comprise an antimildew contact fungicide.
7. Compositions according to claim 6, wherein the antimildew contact fungicide is folpet.
8. Compositions according to claim 6, wherein the antimildew contact fungicide is captafol.
- 30 9. Compositions according to claim 6, wherein the antimildew contact fungicide is mancozeb.
10. Compositions according to claim 6, wherein the contact fungicide is based on copper.
11. Compositions according to any one of claims 1 to 10 which comprise from 0.001 to 95% by weight of active ingredient.
12. Compositions according to any one of claims 1 to 11 which comprise from 0.1% to 20% by weight of surface-active agent.
- 35 13. Compositions according to any one of claims 1 to 12 in the form of dusting or sprinkling powders, granules, solutions, water-soluble concentrates, emulsifiable concentrates, emulsions, suspension concentrates, aerosols, wettable powders and pastes.
14. Compositions according to any one of claims 1 to 10 in the form of dusting or sprinkling powders.
- 40 15. Compositions according to any one of claims 1 to 10 in the form of emulsifiable or water-soluble concentrates comprising from 10 to 80% by weight of active ingredient.
16. Compositions according to any one of claims 1 to 10 in the form of emulsions or solutions comprising from 0.001 to 20% by weight of active ingredient.
17. Compositions according to any one of claims 1 to 10 in the form of suspension concentrates
- 45 comprising from 10 to 75% by weight of active ingredient, from 0.5 to 15% by weight of surface-active agent, from 0.1 to 10% by weight of thixotropic agent, from 0 to 10% by weight of suitable additives and, as carrier, water or an organic liquid in which the active ingredient is sparingly soluble or insoluble.
18. Compositions according to any one of claims 1 to 10 in the form of wettable powders comprising from 20 to 95% by weight of active ingredient, from 0 to 5% by weight of a wetting agent, from 3 to 10% by weight of a dispersing agent, from 0 to 10% by weight of one or more stabilisers and/or other additives, and a solid carrier.
- 50 19. Compositions according to any one of claims 1 to 10 in the form of granules having dimensions of between 0.1 and 2 mm and comprising from 0.5 to 25% by weight of active ingredient and from 0 to 10% by weight of additives.
- 55 20. Fungicidal compositions according to claim 1 substantially as hereinbefore described.
21. Fungicidal compositions according to claim 1 substantially as hereinbefore described in Example 2 or

- 3.
22. A method for treating plants against attack by phytopathogenic fungi, which comprises applying to these plants an effective amount of a mixture of A) at least one compound of general formula I depicted in claim 1 (wherein R, M and n are as defined in claim 1) and B) 1-(2-cyano-2-methoxyiminoacetyl)-3-methylurea in a composition according to any one of claims 1 to 21. 5
23. A method according to claim 22 in which the composition is applied after contamination of the plants with the fungus or fungi.
24. A method according to claim 22 for treating plants against attack by phytopathogenic fungi substantially as hereinbefore described.
- 10 25. A method according to claim 22 for treating plants against attack by phytopathogenic fungi substantially as hereinbefore described in Example 1. 10



US005169646A

United States Patent [19]

Horriere et al.

[11] Patent Number: **5,169,646**[45] Date of Patent: **Dec. 8, 1992**[54] **FUNGICIDAL COMPOSITIONS BASED ON ALKYL PHOSPHITES**

4,436,744 3/1984 Harr 424/141

[75] Inventors: **Daniel Horriere**, Fontaines S/Saone;
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France[73] Assignee: **Rhone-Poulenc Agrochimie**, Lyon,
France[21] Appl. No.: **839,057**[22] Filed: **Feb. 18, 1992****Related U.S. Application Data**

[60] Continuation of Ser. No. 611,437, Nov. 7, 1990, abandoned, which is a continuation of Ser. No. 250,937, Sep. 29, 1988, abandoned, which is a division of Ser. No. 196,759, May 17, 1988, Pat. No. 4,806,445, which is a continuation of Ser. No. 897,156, Aug. 18, 1986, abandoned, which is a division of Ser. No. 357,567, Mar. 12, 1982, Pat. No. 4,698,334, which is a continuation-in-part of Ser. No. 133,143, Mar. 24, 1980, abandoned, which is a continuation of Ser. No. 869,234, Jan. 13, 1978, abandoned.

[30] **Foreign Application Priority Data**

Jan. 14, 1977 [FR] France 77 01639

[51] Int. Cl.⁵ **A01N 57/18; A01N 59/20**[52] U.S. Cl. **424/632; 424/630; 424/633; 424/635; 424/637; 424/638; 514/141**[58] Field of Search **514/141; 424/630, 632, 424/633, 635, 637, 638**[56] **References Cited****U.S. PATENT DOCUMENTS**

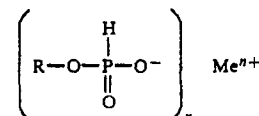
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OTHER PUBLICATIONS

Frear, Chemistry of the Pesticides, pp. iii and 316-331.

Primary Examiner—Allen J. Robinson*Attorney, Agent, or Firm*—Emmanuel J. Lobato; Robert E. Burns[57] **ABSTRACT**

A fungicidal composition and method for the protection of vines against disease are provided. The composition which is applied to vines contains as active material a mixture of 1 part by weight of a monoester salt of a phosphorous acid of the formula



in which

R is an alkyl radical having 2 to 4 carbon atoms

Me is an alkali metal, alkaline earth, or aluminum atom

n is a whole number from 1 to 3 equal to the valence of Me

and from 0.05 to 8 parts of at least one contact fungicide selected from the group consisting of compounds having a base of copper, the metallic ethylene bisdithiocarbamates, and the derivatives of phthalimide.

2 Claims, No Drawings

FUNGICIDAL COMPOSITIONS BASED ON ALKYL PHOSPHITES

REFERENCE TO RELATED APPLICATIONS

This application is a continuation of Ser. No. 6111,437, filed Nov. 7, 1990, and now abandoned, which is a continuation of Ser. No. 250,937, filed Sep. 29, 1988, now abandoned, which is a division of Ser. No. 196,759, filed May 17, 1988, now U.S. Pat. No. 4,806,445, which is a continuation of Ser. No. 897,156, filed Aug. 18, 1986, and now abandoned, which is a division of Ser. No. 357,567, filed Mar. 12, 1982, now U.S. Pat. No. 4,698,334, which is a continuation-in-part of Ser. No. 133,143, filed Mar. 24, 1980 now abandoned, which is a continuation of Ser. No. 869,234, filed Jan. 13, 1978 and now abandoned.

BACKGROUND OF INVENTION

The present invention relates to fungicidal compositions having a base of metallic alkyl phosphites for the protection of vines, in particular against mildew, as well as a process for the antifungal treatment of vines by means of these compositions.

Fungicidal compositions based on alkyl phosphites which can be employed, in particular, for protecting vines from mildew have been proposed in U.S. Pat. No. 4,139,616 of Ducret et al. The active material of these compositions is described as having a systemic action, in contradistinction to previous antimildew fungicides; that is to say, the active material is carried from its point of application on the leaves to the other parts of the plant by the sap.

More thorough experimentation with these new fungicides on vines has shown that alkyl phosphites provide excellent protection of vine leaves against mildew, i.e. *Plasmopora viticola*, during the first months of vegetation, but that their fungicidal activity decreases substantially when the leaves become senescent. Thus, starting with the month of August, a progressive invasion is found by mildew on the old leaves, which are generally located at the base of the vine, while the rest of the foliage which has been more recently formed remains protected as a result of the systemic action of the alkyl phosphite based fungicide.

Certain conventional antimildew fungicides of the metallic ethylene-bis-dithiocarbamate type or derivatives of phthalimides exhibit good persistence on the vine but are not considered to have systemic activity.

SUMMARY OF THE INVENTION

An object of the present invention is a fungicidal composition which provides persistent protection for plants against fungal infection, especially mildew.

Another object of the present invention is a fungicidal composition which provides protection for plants, especially vine plants, against fungal infection that is more lasting than that provided by previous alkyl phosphite antifungal compositions.

A further object of the present invention is a method of treating plants to provide protection against mildew which lasts for an entire season.

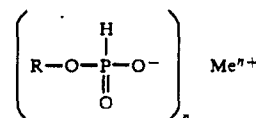
Still a further object of the present invention is a composition for treating plants wherein the amount of an active agent used is less than that required in prior compositions to provide a protection against fungal infection.

These and other objects are obtained by the invention disclosed below.

It has been found surprisingly, that excellent antimildew protection for the entire season is obtained when the vine is treated with mixtures of special alkyl phosphites and certain known antimildew agents having contact action, in which at least one of the active materials is present in an amount far less than that recommended when employed alone for the same use.

According to the invention, fungicidal compositions for the protection of vines, especially against mildew, contain as active material

a monoester of phosphorous acid of the formula



in which:

R is an alkyl radical containing from 2 to 4 carbon atoms,

Me is an alkali metal, alkaline earth metal, or aluminum atom, and

n is a whole number from 1 to 3, equal to the valence of Me,

in combination with

a contact fungicide selected from

(a) fungicidal compositions having a base of copper such as copper oxychloride, copper sulfate neutralized with slaked lime and cuprous oxide,

(b) metallic ethylene bisdithiocarbamates, such as maneb (manganese ethylene bisdithiocarbamate), mancozeb (manganese-zinc ethylene bisdithiocarbamate), and

(c) phthalimide type fungicides, such as captafol or N-(1,1,2,2-tetrachloroethylthio)-1,2,3,6-tetrahydrophthalimide and folpel, or folpet, or N-(trichloromethylthio)phthalimide, in which at least one of the active fungicidal materials is present in the mixture in an amount substantially less than that in which it is currently used by itself for the same purpose.

DESCRIPTION OF THE INVENTION

More precisely, the compositions of the invention which contain a mixture of at least one salt of a monoester of phosphorous acid of the above formula and at least one contact fungicide are effective antifungal agents when applied in an amount in which the individual constituents are present in amounts of about 15% to 75% of the doses recommended for use when the constituents are applied by themselves. The relative proportions of each of the components of the composition of the invention are such that the mixtures have remarkable and unexpected synergistic characteristics.

Desirably, the instant compositions are applied by spraying and compositions useful for spraying including compositions containing an agriculturally acceptable carrier are included among the compositions of the invention.

Particularly, significant and interesting results have been obtained in the case of mixtures containing 0.05 to 8 parts of contact fungicides to 1 part of alkyl phosphite. These mixtures, applied by leaf spraying, contain gener-

ally from 50 to 400 g./hl. of alkyl phosphite and from 20 to 400 g./hl. of contact fungicide.

Among the particularly preferred compositions are those which comprise calcium ethyl phosphite and a contact fungicide selected from folpel, copper oxychloride, Bordeaux mixture, mancozeb or captafol; the preferred ratios by weight of calcium ethyl phosphite to contact fungicide in such compositions are approximately 1:0.5, 1:0.8, 1:0.8, 1:0.6 and 1:0.33, respectively. Also preferred are compositions comprising aluminum ethyl phosphite and folpel, preferably in a ratio by weight of about 1:0.5.

The above-mentioned compositions are useful for the treatment of vines against fungus infection, for example, mildew.

The following examples illustrate the synergistic behavior of the fungicidal mixtures in accordance with the invention, however, the examples are not to be construed as limiting the invention in any manner.

EXAMPLE 1

Several series of 10 vine stocks (Gamay variety) were subjected, from the spring until the beginning of August with watering in a very fine spray regularly, so as to cause a heavy contamination with mildew.

The vines were treated 8 times from May 12 to August 12 at intervals of 12 days on the average with a dispersion of wettable powders or solution of soluble powders of active materials consisting either of alkyl phosphites alone or of contact fungicides alone or else mixtures, formed just prior to use, of these two types of components. The spraying was effected by means of sprayers with deliveries of the order of 800 L/h.

The development of the attack of mildew on the foliage was checked and countings of the infested surface of the leaves were carried out regularly.

For each counting, the percentage contamination of the surface of the treated leaves is evaluated and referred to the percentage contamination of the surface of the control vines which were contaminated under the same conditions. This contamination ratio is then expressed in percent. The difference between the number obtained and 100 is then determined in order to express the percentage of protected surface.

The following results are given as of the end of September. This period is selected as being sufficiently late to be able to judge the intensity and persistence of the effectiveness close to the end of the season, at the time when the control vine are practically completely infested, but before the defoliation of the vines. It is, however, clear that under these conditions the surface of contamination foliage corresponds substantially to that of the foliage treated.

The doses are expressed in grams of active material/hectoliter, those concerning the copper-base compounds being expressed as metallic copper.

The active materials appearing in the examples are the following:

copper oxychloride, applied as a wettable powder, 50% copper,

Bordeaux mixture having a base of copper sulfate with 20% copper, neutralized with slaked lime,

maneb: manganese ethylene bisdithiocarbamate, applied as a wettable powder with 80% active substance,

mancozeb: manganese-zinc ethylene bisdithiocarbamate (2.5%) as wettable powder with 8% active material,

captafol: N-(1,1,2,2-tetrachloroethylthio)-1,2,3,6-tetrahydrophthalimide, as wettable powder, 80% active material,

folpel or folpet: N-(trichloromethylthio)phthalimide, applied as wettable powder of 50% active material.

The synergism is evaluated on basis of these results by way of comparison between the protected surface S_m obtained with the mixture and the sum of the protected surfaces S_p and S_c obtained with the alkyl phosphite and the contact fungicide respectively, taken separately.

If the value S_m is greater than this sum, the effect is superior to what could be theoretically expected from the action of the mixture if the properties were simply additive; there is thus synergism.

Finally, in most cases, the action of the known fungicidal compound, used in its recommended dose, is indicated by way of memorandum at the top of each table. In order to make this synergism clearer, the sum $S_p + S_c$ is indicated between parenthesis after the value S_m .

TABLE 1

MIXTURES WITH SODIUM ETHYL PHOSPHITE Used As Soluble Powder With 80% Active Substance		
Sodium ethyl-phosphite g./hl.	Contact Fungicide g./hl.	% on September 26 of protected surface of leaves treated
250	copper oxychloride	S_p 4
—	80	S_c 10
250	80	S_m 60 ($S_p + S_c = 14$)
—	maneb	
—	280 (Recom. dose) for use	54
250	—	S_p 4
—	125	S_c 36
250	125	S_m 46 ($S_p + S_c = 40$)
—	captafol	
—	160 (Recom. dose) for use	70
250	—	S_p 4
—	50	S_c 30
250	50	S_m 55 ($S_p + S_c = 34$)
—	folpel	
—	150 (Recom. dose) for use	54
250	—	S_p 4
—	100	S_c 25
250	100	S_m 58 ($S_p + S_c = 29$)

TABLE 2

MIXTURES HAVING A BASE OF ALUMINUM ETHYL PHOSPHITE Used As Wettable Powder With 80% Active Material		
Aluminum ethyl-phosphite g./hl.	Contact Fungicide g./hl.	% on September 26 of protected surface of leaves treated
—	copper oxychloride	
—	500 (Recom. dose) for use	90
250	—	S_p 5
—	120	S_p 12
250	120	S_m 60 ($S_p + S_c = 17$)
—	maneb	
—	280 (Recom. dose) for use	54
200	—	S_p 4
—	200	S_c 44
200	200	S_m 56 ($S_p + S_c = 48$)
—	captafol	
—	160 (Recom. dose) for use	70
250	—	S_p 5
—	50	S_c 30
250	50	S_m 50 ($S_p + S_c = 35$)
—	folpel	

TABLE 2-continued

MIXTURES HAVING A BASE OF ALUMINUM ETHYL PHOSPHITE Used As Wettable Powder With 80% Active Material		
Aluminum ethyl- phosphite g./hl.	Contact Fungicide g./hl.	% on September 26 of protected surface of leaves treated
—	150 (Recom. dose) for use	54
250	—	Sp 5
—	100	Sc 25
250	100	Sm 56 (Sp + Sc = 30)

Moreover, during the course of these tests, there could be noted the excellent activity of a mixture of aluminum ethyl phosphite and folpel against excoriosis (*Phomopsis viticola*), blackrot (*Guignardia bidwelli*), brenner (*Pseudopeziza tracheifila*) as well as the retarding action on oidium (*Uncinula necator*).

EXAMPLE 3

TABLE 3

MIXTURES HAVING A BASE OF MAGNESIUM ISOPROPYL PHOSPHITE Used As A Soluble Powder With 50% Active Material		
Magnesium iso- propyl phosphite g./hl.	Contact Fungicide g./hl.	% on September 26 of protected surface of leaves treated
—	<u>copper oxychloride</u> 500 (Recom. dose) for use	90
250	—	Sp 4
—	120	Sc 12
250	120	Sm 50 (Sp + Sc = 16)
—	<u>maneb</u> 280 (Recom. dose) for use	54
200	—	Sp 4
—	200	Sc 44
200	200	Sm 56 (Sp + Sc = 48)
250	—	Sp 4
—	125	Sp 36
250	125	Sm 44 (Sp + Sc = 40)
—	<u>captafol</u> 160 (Recom. dose) for use	70
250	—	Sp 4
—	50	Sc 30
250	50	Sm 60 (Sp + Sc = 34)
—	<u>folpel</u> 150	54
250	—	Sp 4
—	100	Sc 25
250	100	Sm 50 (Sp + Sc = 29)

EXAMPLE 4

TABLE 4

MIXTURES HAVING A BASE OF CALCIUM ISOPROPYL PHOSPHITE Used As Soluble Powder With 80% Active Material		
Calcium iso- propyl phosphite g./hl.	Contact Fungicide g./hl.	% on September 26 of protected surface of leaves treated
—	<u>maneb</u> 280 (Recom. dose) for use	54
250	—	Sp 4
—	125	Sp 36
250	125	Sm 46 (Sp + Sc = 40)
—	<u>folpel</u> 150	54
250	—	Sp 4
—	100	Sc 25

TABLE 4-continued

MIXTURES HAVING A BASE OF CALCIUM ISOPROPYL PHOSPHITE Used As Soluble Powder With 80% Active Material		
Calcium iso- propyl phosphite g./hl.	Contact Fungicide g./hl.	% on September 26 of protected surface of leaves treated
250	100	Sm 54 (Sp + Sc = 29)

EXAMPLE 5

TABLE 5

MIXTURES WITH ALUMINUM ISOPROPYL PHOSPHITE Used As Wettable Powder With 80% Active Material		
Aluminum iso- propyl phosphite g./hl.	Contact Fungicide g./hl.	% on September 26 of protected surface of leaves treated
—	<u>copper oxychloride</u> 500 (Recom. dose) for use	90
250	—	Sp 4
—	120	Sc 12
250	120	Sm 50 (Sp + Sc = 16)
—	<u>maneb</u> 280 (Recom. dose) for use	54
200	—	Sp 4
—	200	Sc 34
200	200	Sm 54 (Sp + Sc = 38)
—	<u>captafol</u> 160 (Recom. dose) for use	70
250	—	Sp 4
—	50	Sc 30
250	50	Sm 50 (Sp + Sc = 34)
—	<u>folpel</u> 150 (Recom. dose) for use	54
250	—	Sp 4
—	100	Sc 25
250	100	Sm 50 (Sp + Sc = 29)

EXAMPLE 6

Tests under conditions of treatment very close to those described in Example 1 were carried out in another year with preformulated mixtures having a base of aluminum ethyl phosphite and mancozeb, each of the components being used in doses far less than the normal doses of use. The results, expressed as previously, are set forth in Table 6:

TABLE 6

MIXTURES WITH ALUMINUM ETHYL PHOSPHITE		
Aluminum ethyl- phosphite g./hl.	Contact Fungicide g./hl.	% on September 27 of protected surface referred to the surface treated
—	<u>mancozeb</u> 280 (Recom. dose) for use	85
150	—	Sp 22
—	90	Sc 64
150	90	Sm 96 (Sp + Sc = 86)
175	—	Sp 25
—	100	Sc 65
175	100	Sm 96 (Sp + Sc = 90)
—	<u>cupric oxychloride</u> 75	Sp 34
150	—	Sc 21
150	75	Sm 79 (Sp + Sc = 55)
—	100	Sp 45
200	—	Sc 32
200	100	Sm 87 (Sp + Sc = 77)
—	Bordeaux mixture	

TABLE 6-continued

MIXTURES WITH ALUMINUM ETHYL PHOSPHITE		
Aluminum ethyl-phosphite g./hl.	Contact Fungicide g./hl.	% on September 27 of protected surface referred to the surface treated
with 20% metallic copper		
—	75	Sp 34
150	—	Sc 21
150	75	Sm 93 (Sp + Sc = 55)
cuprous oxide		
—	75	Sp 34
150	—	Sc 21
150	75	Sm 87 (Sp + Sc = 55)

Excellent protection of the vine up to the end of the season was obtained by applying to it, either in pre-prepared mixture or in mixture formed on the spot, compositions having a base of the above mixtures associated with another contact fungicide. This applies in particular to compositions containing:

from 80 to 150 g./hl. of aluminum ethyl phosphite
from 40 to 60 g./hl. of folpet
from 60 to 80 g./hl. of mancozeb
from 130 to 240 g./hl. of copper.

Similar results are obtained when the alkyl phosphites tested are replaced in the mixtures by the following compounds:

magnesium ethyl phosphite
magnesium isobutyl phosphite
magnesium sec.butyl phosphite
calcium isobutyl phosphite
aluminum N-butyl phosphite
aluminum sec.butyl phosphite
aluminum isobutyl phosphite.

EXAMPLE 7

Several series of 10 vine-stocks (Gamay variety) were subjected from spring to the start of August, to regular watering by very fine spray, so as to cause severe combination with mildew (*plasmopora viticola*).

The vine-stocks were treated 9 times, from May 30th to August 22nd at average intervals of 11 days, with dispersions of wettable powders or solutions of soluble powders of active materials consisting either solely of calcium ethyl phosphite or solely of contact fungicides or of mixtures, prepared just before use, of these two types of constituents. Spraying was carried out by means of sprayers delivering of the order of 800 l/ hectare. The development of the mildew attack on the foliage was observed and counts of the invaded surface of the leaves were made regularly.

For each count are estimated over the total surface of the leaves, the percentage of contamination of the surface of the treated leaves S_x and that of the surface of the control vine-stocks S_T , the latter having been contaminated under the same conditions. Thereafter, a coefficient of efficacy is calculated using the formula

$$\frac{S_T - S_x}{S_T}$$

The results given in the Tables 7 and 8 are given for a count at the beginning of October.

This period is selected as being sufficiently late to be able to judge the intensity and persistence of the effectiveness of the various treatments close to the end of the

season, at a time when the controls are practically completely infested, but before the defoliation of the vines.

The doses are expressed in g. of active material/hl., those relating to the compounds based on copper being expressed in terms of copper metal.

The active materials (a.m.) used are the following: calcium ethyl phosphite as a wettable powder having the following composition by weight:

calcium ethyl phosphite	80%
calcium lignosulphate	4%
sodium isopropyl-naphthalene sulphonate	4%
kaolin	12%

folpet: N-(trichloromethylthio)phthalimide as a wettable powder containing 50% by weight of active material

copper oxychloride as a wettable powder containing 50% by weight of copper

Bordeaux mixture based on copper sulphate neutralized with calcium hydroxide, and containing 20% by weight of copper.

The synergism is evaluated on the basis of these results by comparison between the coefficient of efficacy Sm obtained with the mixture and the sum of the coefficients of efficacy Sp and Sc obtained with the ethyl-phosphite and the contact fungicide used separately.

If the value Sm is greater than the sum, Sp+Sc, the effect is superior to what could be theoretically expected from the action of the mixture if the properties of the components were simply additive; there is thus synergism. In order to make this synergism clearer, the sum Sp+Sc is indicated between parenthesis after the value Sm.

TABLE 7

MIXTURES WITH CALCIUM ETHYL PHOSPHITE		
Calcium ethyl phosphite g.a.m.	Contact fungicide g.a.m.	Coefficient of efficacy on 3rd October
folpet		
150	—	Sp 18
—	75	Sc 37
150	75	Sm 86 (Sp + Sc = 55)
copper oxychloride		
150	—	Sp 18
—	120	Sc 43
150	120	Sm 71 (Sp + Sc = 61)
Bordeaux mixture		
150	—	Sp 18
—	120	Sc 41
150	120	Sm 72 (Sp + Sc = 59)

EXAMPLE 8

Another year a field trial is carried out using the same procedure as that described in Example 7, with the following particular conditions:

the vine-stocks are treated 8 times from May 31 up to

August 9, at an average interval of 10 days:

the active materials tested are as follows:

calcium ethyl phosphite	80%
calcium lignosulphate	4%
sodium isopropyl-naphthalene sulphonate	4%
kaolin	12%

mancozeb: manganese and zinc (2.5% w/w) ethylene-bisdithiocarbamate as a wettable powder containing

80% w/w of active ingredient captafol: N-(1,1,2,2-tetra-chloroethylthio)-1,2,3,6-tetrahydrophthalimide as a suspension concentrate containing 480 g./l. of active material.

The results are expressed in Table 8 in the same way as in Example 7.

TABLE 8

MIXTURES WITH CALCIUM ETHYL PHOSPHITE		
Calcium ethyl phosphite	Contact fungicide g.a.m./hl.	Coefficient of efficacy on October 1
	<u>mancozeb</u>	
150	—	Sp 9
—	90	Sc 58
150	90	Sm 83 (Sp + Sc = 67)
	<u>captafol</u>	
150	—	Sp 9
—	50	Sc 62
150	50	Sm 86 (Sp + Sc = 71)

EXAMPLE 9

The test described below illustrates the synergistic behavior of a fungicidal composition according to the invention comprising aluminum ethyl phosphite and folpel in a ratio of 1:0.5 by weight.

Several series of 10 vine-stocks (Gamay variety) were subjected, from spring to the start of August, to regular watering by very fine spray, so as to cause severe contamination with mildew (*plasmopara viticola*).

The vine-stocks were treated 8 times from May 31 to August 9, at average intervals of 10 days, with dispersions of wettable powders or solutions of soluble powders of active materials consisting either solely of alkyl phosphite or solely of contact fungicide or of a mixture, prepared just before use, of these two constituents. Spraying was carried out by means of sprayers delivering of the order of 800 l/hectare. The development of the mildew attack was observed and counts of the invaded surface were made regularly.

For each count are estimated over the total surface of the leaves the percentage of contamination of the surface of the treated leaves S_x and that of the surface of the control vine-stocks S_T , the latter having been contaminated under the same conditions. Thereafter a coefficient of efficacy is calculated using the formula

$$\frac{S_T - S_x}{S_T}$$

The results in Table 9 given for a count at the end of September.

This period is selected as being sufficiently late to be able to judge the intensity and persistence of the effectiveness of the various treatments close to the end of the season, at a time when the controls are practically completely infested, but before the defoliation of the vines.

The dose are expressed in grams of active material/hectoliter. The contact fungicide appearing in the Test is folpel or folpet, i.e. N-(trichloromethylthio)phthalimide, applied as a wettable powder containing 50% w/w active material.

The synergistic effect is evaluated on the basis of these results by comparison of the coefficient of efficacy Sm obtained with the mixture and the sum of the coefficients of efficacy Sp and Sc obtained with the alkyl phosphite and the contact fungicide respectively, taken separately.

If the value Sm is greater than this sum, the effect is superior to what could theoretically be expected from the action of the mixture if the properties were simply additive; there is thus synergism. In order to make this synergism clearer, the sum Sp + Sc is indicated in parenthesis after the value Sm.

TABLE 9

MIXTURES BASED ON ALUMINUM ETHYL PHOSPHITE			
Ratio contact fungicide/alkyl phosphite	Aluminum ethyl-phosphite g./hl.	Folpel g./hl.	Coefficient of efficacy on 26th September
0.5/1	200	—	Sp 4
	—	100	Sc 25
	200	100	Sm 56 (Sp + Sc = 29)

All these examples clearly show that:

On the one hand, the protective action of the alkyl phosphites alone on the aged leaves, that is to say the treated foliage, is insufficient due to a lack of permanence. These compounds therefore cannot be used by themselves to assure protection of the treated foliage up to the end of the season.

On the other hand, the contact fungicides in their recommended dose assure a certain amount of protection which may be excellent, as in the case of the copper-base compounds. However, as soon as the doses are substantially decreased, the action of the products, still considered residual, becomes very greatly reduced, to the point of making them ineffective in these doses.

Knowing thus that the alkyl phosphites assure good protection at the start of the season and the contact fungicides good protection for the rest of the season, one could have expected an action which was merely complementary in time. It is completely surprising that at the end of the season, the protection of foliage treated with compositions of the invention has been found to be not only superior to that of the contact fungicides used by themselves, but far superior to the theoretical sum of the protections which are obtained with each of the components taken individually in the same doses as in the mixture.

The synergism noted is observed for a given selection of alkyl phosphites with certain contact fungicides, preferably with compounds having a base of copper, mancozeb and folpel.

The fungicidal compositions in accordance with the invention, contain as active material, a mixture comprising from 0.5 to 8 and preferably from 0.1 to 2 parts by weight of contact fungicides per part of alkyl phosphite. The compositions are applied preferably by leaf spraying in an amount of 50 to 400 g./hl. of contact fungicide.

More precisely, the copper base mixtures contain 0.15 to 2 parts of metallic copper per part of alkyl phosphite.

The mixtures having a base of metallic ethylene bisdithiocarbamate contain from 0.2 to 2 parts of these fungicides per part of alkyl phosphite.

The mixtures having a base of phthalimide derivatives contain from 0.1 to 1.2 parts of these fungicides per part of alkyl phosphite.

The ternary mixtures, that is to say, mixtures containing two contact fungicides, contain by weight preferably from 0.25 to 0.75 part of phthalimide derivatives or 0.4 to 1 part of metal ethylene bisdithiocarbamate and 0.85 to 3 parts of metallic copper per part of ethyl phosphite.

For their use in practice, the mixtures in accordance with the invention are rarely used alone. Generally, they are part of formulations which, in most cases, include in addition to the active material of the invention, also a carrier or support and/or a surface-active agent.

The expression "carrier" or "support" within the meaning of the present specification refers to an organic or inorganic material, natural or synthetic, with which the active material is associated to facilitate its application to the plant, the seeds, or the soil, or its transportation or handling. The support may be solid (clays, natural or synthetic silicates, resins, waxes, solid fertilizers) or liquid (water, alcohols, ketones, petroleum fractions, chlorinated hydrocarbons, liquified gases).

The surface-active may be an emulsifying, dispersing, or wetting agent, whether ionic or nonionic. Mention may be made, by way of example of salts of polyacrylic acids, lignin-sulfonic acids, ethylene oxide condensates with fatty alcohols, fatty acids, or fatty amines.

The compositions in accordance with the invention can be prepared in the form of wettable powders, soluble powders, solutions, emulsifiable concentrates, emulsions, concentrates in suspension, and suspensions.

The wettable powders are customarily prepared in such a manner that they contain from 20 to 95% by weight of material and they customarily contain, in addition to a solid support, from 0 to 5% by weight of wetting agent, from 3 to 10% by weight of a dispersing agent, and, when necessary, from 0 to 10% by weight of one of more stabilizers and/or other additives, such as penetration agents, adhesives, or anti-clodding agents, coloring substances, etc. By way of example the composition of a wettable powder is given herewith:

active material	50%
calcium lignosulfonate (deflocculant)	5%
anionic wetting agent (alkaline alkyl naphthalene sulfonate)	1%
anticlodding silica	5%
kaolin (filler)	39%

The water soluble powders are obtained by mixing 20 to 95% by weight of active material, 0 to 10% of an anticlodding filler and 0 to 1% of a wetting agent, the balance consisting of a water-soluble filler, primarily a salt.

An example of the composition of a water soluble powder follows:

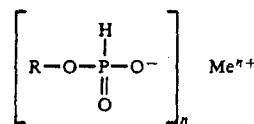
active material	80%
anionic wetting agent (alkaline alkyl naphthalene sulfonate)	0.5%
anticlodding silica	4%
sodium sulfate (soluble filler)	15.5%

Aqueous dispersions and emulsions, for instance the compositions obtained by diluting with water a wettable powder or an emulsifiable concentrate in accordance with the invention, are included within the general scope of the present invention. These emulsions may be of the water-in-oil type or of the oil-in-water type and they may have a thick consistency like that of mayonnaise.

What we desire to claim and protect by Letters Patent is:

1. A fungicidal composition for the protection of plants against fungal diseases, which comprises as the active material a mixture of:

1 part by weight of a monoester salt of a phosphorous acid of the formula



in which

R is an alkyl radical having 2 to 4 carbon atoms, Me is an alkali metal, alkaline earth metal or aluminum atom, and

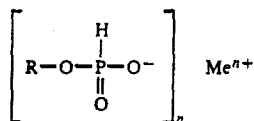
n is a whole number from 1 to 3 equal to the valence of Me,

at least one copper containing contact fungicide selected from a member of the group consisting of copper oxychloride, copper sulfate neutralized by calcium hydroxide and copper oxide, in an amount such that the mixture contains about 0.85 to 3 parts by weight of copper, expressed as metallic copper, per part by weight of alkyl phosphite salt and

an additional contact fungicide selected from a member of the group consisting of a metallic ethylene bisdithiocarbamate in an amount of about 0.4 to 1 part by weight per part by weight of alkyl phosphite salt and a fungicidal phthalimide compound in an amount of about 0.25 to 0.75 part by weight per part by weight of alkyl phosphite salt, wherein the metallic ethylene bisdithiocarbamate is manganese ethylene bisdithiocarbamate or manganese-zinc ethylene bisdithiocarbamate and the fungicidal phthalimide compound is N-(1,1,2,2-tetrachloroethylthio)-1,2,3,6-tetrahydrophthalimide or N-(trichloromethylthio)phthalimide.

2. A fungicidal composition for the protection of plants against fungal diseases which comprises as the active material a mixture of:

1 part by weight of a monoester of a phosphorous acid of the formula



in which

R is an alkyl radical having 2 to 4 carbon atoms, Me is an alkali metal, alkaline earth metal or aluminum atom and

n is a whole number from 1 to 3 equal to the valence of Me, and

at least one copper containing contact fungicide selected from a member of the group consisting of copper oxychloride, copper sulfate neutralized by calcium hydroxide and copper oxide, in an amount such that the mixture contains about 0.3 to 2 parts by weight of copper, expressed as metallic copper, per part by weight of alkyl phosphite salt.

* * * * *

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES**

202085
Bogotá, D.C.,

Abogado
✓ **ALVARO CORREA ORDOÑEZ**

ASUNTO	Radicación	06095708
	Trámite	011
	Evento	378
	Actuación	519
	Oficio	<u>11</u> 05312
	Folios	22

Patente de Invención	☒	Patente de Modelo de Utilidad	☐
Vía Nacional	☐		
Vía PCT (fase nacional)	☒	Cap. I	☒
		Cap. II	☐

No. Sol. Internacional: PCT/EP2005/002880
Fecha de Presentación Internacional: 2005-02-23

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

Capitulo descriptivo: Folios 19 a 34 y 36 tal y como fueron presentados.
Capitulo reivindicatorio: Folio 35 tal y como fueron presentados.
Prioridad: Folio 1 EP04356025,9 2004-02-25.

2. Objeto de la invención

Título de la solicitud: Composición fungicida que comprende un derivado de ácido fosforoso y tolilfluanida ó diclofluanida. Folio 1.

Objeto de la invención: El objeto de la presente solicitud de patente de invención se refiere a una composición fungicida que comprende un derivado de ácido fosforoso y tolilfluanida ó diclofluanida.

La presente solicitud de patente indica que algunos derivados de acido fosforoso, tolilfluanida ó diclofluanida se conocen como compuestos fungicidas individuales. Sin embargo no se ha informado de combinaciones de éstos ó de combinaciones fungicidas que combinan estos compuestos

3. De la solicitud de Patente

El solicitante debe modificar el título de la invención de tal forma que indique específicamente la materia objeto de invención.

3.1. Reivindicaciones (artículo 30 D 486)

El capítulo reivindicatorio corresponde a una generalización sin sustento en la descripción. En primer lugar el componente definido como "un derivado de ácido fosforoso" no define específicamente ningún derivado. Y en segundo lugar la inclusión de la diclofluanida también es una generalización sin sustento, pues que los resultados mostrados en la descripción, corresponden únicamente a combinaciones de fosetil con tolilfluanida, en proporciones definidas.

El solicitante debe definir específicamente en la reivindicación independiente la materia y el alcance de la invención. Los cuales a su vez deben estar enteramente sustentados allí.

En conclusión, el capítulo reivindicatorio no cumple con el requisito de concisión y sustento en la descripción de acuerdo al art. 30 de la Decisión 486 o art.22 Tratado PCT.

4. **Reivindicaciones relativas a un uso o a un segundo uso** (artículos 14 y 21 D 486)

Aunque las reivindicaciones 7 a 10 se presentan como reivindicaciones de método, estas hacen referencia al uso de la composición fungicida de la reivindicación 1 para la lucha contra los hongos fitopatógenicos de los cultivos agrícolas. Es evidente que la llamada etapa de "se aplica" corresponde a la forma de usar la composición. Por lo tanto dicho método no es patentable a partir del artículo 14 de la Decisión 486.

Se le aclara al solicitante que un método cuya única etapa es una aplicación corresponde tan solo a una aplicación, y una aplicación es un uso. Sírvese retirar dichas reivindicaciones.

5. Determinación del Estado de la Técnica

Considerando que la fecha de la prioridad de la solicitud internacional PCT es 2004-02-25, se realizó la búsqueda en el estado de la técnica y se encontraron los documentos relacionados a continuación, que pueden afectar la patentabilidad del objeto de la presente solicitud:

Nº	Documento	Título	Fecha de publicación
D1	US3341403	Method of controlling fungi with N-thio-monofluoro-dicloro-methylimides	1967-09-12
D2	GB2131296	Fungicidal compositions	1984-06-20
D3	US5169646	Fungicidal compositions based on alkyl phosphites	1992-12-08

6. Análisis de patentabilidad (artículo 14 D486)

6.1. Nivel Inventivo (artículo 18 D486)

La solicitud de patente en estudio presenta una composición fungicida que comprende:

- A) Un derivado de ácido fosforoso y
- B) Tolilfluanida ó diclofluanida

Cualquiera de los documentos D2 ó D3 divulga composiciones fungicidas que incluyen un derivado de ácido fosforoso (equivalente al de esta solicitud) y otro ingrediente activo fungicida conocido en el arte. El documento D2 por ejemplo incluye el cymoxanil y el folpet; y el documento D3 incluye fungicidas tipo ftalimida como por ejemplo el folpet, entre otros.

Nótese que cualquiera de estos dos documentos ya había divulgado composiciones con actividad fungicida mejorada basadas en derivados de ácido fosforoso, específicamente de fosetil. Y además se habían probado contra el mismo blanco (*plasmopara vitícola*), obteniendo resultados muy buenos.

Pero además hay que tener en cuenta un último aspecto, los derivados del ftalimida como por ejemplo el folpet pertenecen a la misma familia de la tolilfluanida, así como se enseña en el documento D1. En donde se divulgaron toda esa nueva familia fungicidas.

Así las cosas, un técnico medio en la materia combinando las enseñanzas de los documentos D1 y D2 ó D1 y D3, podría plantear una composición como la de esta solicitud donde de combinan derivados de ácido fosforoso con fungicidas conocidos de la misma familia del folpet, por el ejemplo la tolilfluanida.

En consecuencia la composición fungicida de la presente solicitud, se considera como una alternativa obvia para un técnico medio en la materia, no presente un salto cualitativo en la técnica, pues no produce ningún tipo de efecto sorpréndete ni inesperado y carece de nivel inventivo.

Acá simplemente se esta presentado una combinación alternativa de dos fungicidas conocidos, que no solucionan ningún problema técnico y no hacen ningún aporte a la técnica. Es importante aclarar que un eventual sinergismo es un efecto más que evidente para un técnico medio en la materia; pues es ampliamente conocido que al combinar dos ingredientes activos se pueda mejorar su actividad, basta con medirla.

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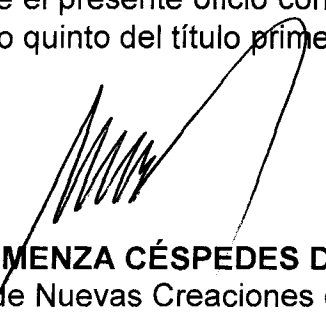
6. Conclusión

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	US3341403	1-6	Nivel Inventivo
D2	GB2131296	1-6	Nivel Inventivo
D3	US5169646	1-6	Nivel Inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


ALIX CARMENZA CÉSPEDES DE VERGEL

Directora de Nuevas Creaciones (C)

El anterior requerimiento fue notificado por fijación en lista, de fecha

23 ABR. 2010

CONCEPTO TÉCNICO No. 1342

EXAMINADOR TÉCNICO

Código No.202085