

PATENT SPECIFICATION

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(54) FUNGICIDAL COMPOSITIONS BASED ON COMPOUNDS WHICH CONTAIN THE PHOSPHITE ANION

(71) We, PHILAGRO formerly known as Pépro, Société pour le Développement et la Vente de Spécialités Chimiques, a body corporate organised under the laws of France, of 14/20, rue Pierre Baizet 69009 Lyon, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fungicidal compositions based on compounds which contain the phosphite anion.

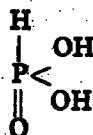
Organic phosphorus compounds with fungicidal properties have already been proposed. In particular certain amino-alkyl phosphates have been described as having interesting effects upon vine mildew. More recently, certain alkyl phosphates have been found to be active with respect to piriculariosis.

We have now found that compositions which contain a compound containing a phosphite anion show outstanding fungicidal properties and may be used as preventive and curative compositions against fungicidal diseases especially in plants.

Accordingly the present invention provides a fungicidal composition comprising as active ingredient a compound which contains the phosphite anion together with a carrier diluent therefor.

By the phrase "compound containing a phosphite anion" we include not only compounds which are ionised on contact with water but also it is envisaged that the active ingredients used in the composition according to the invention may have a systemic activity in which case the phosphite anion may be released within a plant treated by the composition.

Phosphites are salts or esters of phosphorus acid, which is generally represented by the following formula:



In solution the phosphorous acid acts as a diacid and gives two types of anions:

acid phosphites having the anion $[\text{PO}_2\text{H}_2]^-$
neutral phosphites having the anion $[\text{PO}_2\text{H}]^{--}$

Both types of anion necessarily include a hydrogen atom bound to the phosphorus atom. Thus, the present invention is restricted to compositions containing such phosphite anions and to the use of the phosphite anions for preventing or combatting fungal diseases.

Examples of compounds containing the phosphite anion are mineral salts and organic salts which may be mono acid, diacid or neutral salts and may be optionally hydrated.

Examples of suitable salts include salts of alkali metals, such as sodium, lithium, potassium, and salts of ammonium, primary, secondary or tertiary, optionally substituted aliphatic, aromatic, alicyclic or heterocyclic amines or of other nitrogen-containing derivatives (e.g. imidazoles, cyclohexylamine, optionally substituted aniline or morpholine) which are generally readily soluble in water, substantially insoluble or completely insoluble salts such as salts of alkaline earth metals, such as magnesium, calcium, barium, strontium or of heavier metals such as copper, iron, nickel, cobalt, manganese, zinc and aluminium.

These compounds are known *per se*: phosphorous acid and disodium phosphite are commercial products which can be used as starting materials, for producing other salts by conventional processes, such as strong neutralisation or double decomposition.

The invention also provides a method of preventing or combatting a fungus disease which comprises applying to the fungus or to its environment a compound which contains a phosphite anion. It is preferred to apply the active ingredient in the form of a composition according to the invention. The invention is particularly concerned with the treatment of plants.

The following compounds are examples of those tested. The preparation of compounds not commercially available is also given:

- 1 — phosphorous acid H_3PO_3 — m.p. 74°C
- 2 — acid sodium or monosodium phosphite NaH_2PO_3

This salt was prepared by adding an aqueous solution of one equivalent of phosphorous acid to an aqueous solution of one equivalent of soda up to pH 4. The liquid was evaporated until syrupy in consistency and then cooled. The hydrate



crystallised. It is purified by recrystallisation from water.

- 3 — disodium phosphite or neutral sodium phosphite Na_2HPO_3

An aqueous solution of one equivalent of phosphorous acid was added to an aqueous solution of two equivalents of soda up to pH 9. The solution was then crystallised by evaporation. This product corresponds to the formula $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ which becomes deliquescent at 53°C . The hydrate loses its water at 140°C giving the anhydrous phosphite Na_2HPO_3 .

- 4 — acid potassium or monopotassium phosphite KH_2PO_3

This compound was obtained in the same way as compound 2, except that the soda was replaced by potash.

- 5 — neutral potassium phosphite K_2HPO_3

This compound was prepared in the same way as compound 3, except that the soda was replaced by potash. Deliquescent crystals were obtained.

- 6 — acid ammonium phosphite — m.p. 123°C .
- 7 — acid triethyl amine phosphite

This compound was prepared in the same way as compound 2 except that the soda was replaced by triethyl amine.

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8 — *acid monoethanolamine phosphite* $\text{H}_2\text{PO}_3^{\ominus}\oplus\text{H}_2\text{NCH}_2\text{—CH}_2\text{—OH}$

This compound is prepared in the same way as compound 2 except that the soda was replaced by monoethanolamine.

Analysis for $\text{C}_2\text{H}_{10}\text{NO}_4\text{P}$

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	C%	H%	N%	P%
Calculated	16.78	6.99	9.79	21.68
Found	16.91	6.99	9.88	21.67

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9 — *acid calcium phosphite* $\text{Ca}(\text{H}_2\text{PO}_3)_2\cdot\text{H}_2\text{O}$

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This compound was prepared in the same way as compound 2, except that the soda was replaced by calcium carbonate. The solution was evaporated *in vacuo*. The water-soluble crystalline mass loses its water of crystallisation at 150° C.

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10 — *neutral calcium phosphite* $\text{CaHPO}_3\cdot\text{H}_2\text{O}$

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This salt was precipitated by the action of neutral ammonium phosphite on calcium chloride. A white crystalline powder losing its water of crystallisation at 200 to 300° C was obtained.

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11 — *barium diacid phosphite* $\text{BaH}_2(\text{PO}_3\text{H})_2$

This compound was obtained by neutralising phosphorous acid with barium carbonate. The precipitate was filtered and then evaporated to dryness *in vacuo*. The product which was soluble in water decomposes at around 130° C.

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12 — *neutral barium phosphite* BaHPO_3

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This compound was prepared by adding one equivalent of disodium phosphite to one equivalent of an aqueous solution of barium chloride. The neutral phosphite is a salt substantially insoluble in water. Under the effect of heat, it loses one molecule of water between 150 and 200° C. The acid phosphite is reformed by hydrolysing the neutral phosphite in boiling water.

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13 — *neutral copper(II) phosphite* $\text{CuHPO}_3\cdot 2\text{H}_2\text{O}$

Cupric chloride is reacted with ammonium phosphite. The product obtained is a blue, flaky or crystalline material.

14 — *neutral nickel(II) phosphite*

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Nickel(II)chloride was added to phosphorous trichloride partially hydrolysed with ammonia. A precipitate corresponding to the formula $2(\text{NiHPO}_3)\text{H}_2\text{O}\cdot 6\text{H}_2\text{O}$. The product obtained was green in colour and loses about 3 molecules of water in the presence of sulphuric acid. At 250° C, it gives the compound $2(\text{NiHPO}_3)\cdot\text{H}_2\text{O}$.

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15 — *trivalent iron phosphite*

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This compound was obtained by adding ferric chloride to phosphorous acid.

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16 — *manganous phosphite* $\text{MnHPO}_3\cdot\text{H}_2\text{O}$

Phosphorous acid is reacted with manganese(II)carbonate.

Analysis for MnH_3PO_4

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	H%	P%	Mn%
Calculated	1.96	20.25	35.95
Found	1.21	20.17	36.05

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17 — *neutral zinc(II) phosphite* ZnHPO_3

This compound may be obtained by reacting ammonium phosphite with zinc sulphate or by dissolving zinc oxide in phosphorous acid. A compound corresponding

to the formula $\text{ZnHPO}_3 \cdot 15\text{H}_2\text{O}$ is obtained. It loses one molecule of water at 120°C and the rest of its water at 280°C .

18 — *neutral magnesium phosphite* $\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$

This salt was precipitated by the action of one mol of neutral ammonium phosphite on one equivalent of magnesium chloride. After filtration, the salt was obtained in a yield of 68% m.p. above 300°C .

Centesimal analysis for MgHPO_3

%	H	Mg	P
Calculated	6.14	11.30	14.60
Found	6.08	11.39	14.54

19 — *neutral aluminium phosphite* $\text{Al}_2(\text{HPO}_3)_3$

This salt was precipitated by the action of neutral ammonium phosphite on aluminium nitrates. A white precipitate was obtained and was filtered.

20 — *cuprous phosphite* $\text{Cu}_2\text{HPO}_3 \cdot 2\text{H}_2\text{O}$

16.4 g (0.2 mol) of phosphorous acid were mixed with one equivalent of cuprous oxide. The mixture was left to react for one hour. It underwent spontaneous heating and changed colour from red to brown. The precipitate was filtered and the cuprous phosphite obtained in a yield of 97%.

Centesimal analysis for $\text{Cu}_2\text{HPO}_3 \cdot 2\text{H}_2\text{O}$

%	Cu	H	P
Calculated	52.20	2.06	12.80
Found	53.35	2.06	12.84

21 — *acid phosphite of 1,3-imidazole*

16.4 g (0.2 mol) of phosphorous acid were dissolved in 30 ml of water. 13.6 g (0.2 mol) of 1,3-imidazole were then added dropwise with stirring and cooling. This salt was soluble in water: a precipitate was obtained by concentration followed by evaporation. Yield 83%, m.p. 113°C .

Centesimal analysis for $\text{C}_3\text{H}_7\text{N}_2\text{O}_3\text{P}$

%	C	H	N	P
Calculated	24.00	4.67	18.67	20.67
Found	24.06	4.75	18.78	20.68

22 to 27 — *phosphites of organic bases*

The procedure was as in the preceding Example, except that the imidazole was replaced successively by cyclohexylamine, aniline, anilines substituted on the nucleus, in particular by 1 to 3 C_1 — C_4 -alkyl radicals, and morpholine. If the salt obtained is insoluble in water, the crude precipitate was filtered and then recrystallised from water.

The formulae, physical constants (melting point, solubility in water), yield and centesimal analysis were given in the following Table:

Compound No.	Formula	Physical Constants	Yield	Analysis	
				%	Calc. Found
22		m.p: 181°C insoluble	81%	C 41.14 H 5.71 N 8.00 P 17.71	41.06 6.03 8.06 17.66
23		m.p: 207°C insoluble	91%	C 39.78 H 8.84 N 7.73 P 17.13	39.56 9.04 7.79 17.06
24		m.p: 165.5°C insoluble	70%	C 49.77 H 7.37 N 6.45 P 14.29	49.90 7.40 6.44 14.30
25		m.p: 77°C insoluble	41%	C 28.40 H 7.10 N 8.28 P 18.34	28.36 7.12 8.29 18.34
26		m.p: 168°C insoluble	93%	C 49.77 H 7.37 N 6.45 P 14.29	49.94 7.40 6.37 14.34
27		insoluble m.p: -148.3°C	87%	C 49.77 H 7.37 N 6.45 P 14.29	49.98 7.32 6.41 14.30

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The fungicidal properties of the compounds according to the invention are various, but are particularly interesting in the case of vine mildew, as the following Examples show:

EXAMPLE 1: *In vitro* test on mycelian growth.

The compositions according to the invention were studied for their effect on the mycelian growth of the following fungi:

- *Rhizoctonia solani*, responsible for neck canker
- *Botrytis cinerea*, responsible for grey rot
- *Piricularia oryzae*, responsible for piriculariosis in rice.

The "Agar Plate dilution" method is used for each test. A mixture of gelose and an acetone solution or a wettable powder containing the material to be tested in a concentration of 0.25 g/l was poured into a Petri dish at a temperature of approximately 50° C.

The wettable powder is prepared by mixing the following ingredients for 1 minute in a cutting mill:

- | | |
|---|-----|
| — active material to be tested | 20% |
| — deflocculant (calcium lignosulphate) | 5% |
| — wetting agent (sodium alkylaryl sulphonate) | 1% |
| — filler (aluminium silicate) | 74% |

This wettable powder was then mixed with water in a quantity sufficient for application in the required dose.

The gelose-containing mixture was then allowed to solidify, after which mycelian culture discs of the fungus were placed on it.

A Petri dish similar to the preceding Petri dish, except that the gelose-containing medium does not contain any active material, is used as control.

After 4 days at 20° C, the surface area of the inhibition zone observed was evaluated and expressed as a percentage of the inoculated surface area.

Under these conditions, it was found that compound 8 produced 51% and 60% inhibition of *Pythium de Baryanum* and *Rhizoctonia solani*, respectively, and that compound 14 produced 48%, 59% and 78% inhibition of *Botrytis cinerea*, *Piricularia oryzae* and *Rhizoctonia solani*, respectively.

EXAMPLE 2: *In vivo* test on *Plasmopara viticola* in vine plants.

a) *Preventive treatment*

The leaves of pot-grown, vine plants (Gamay variety) was sprayed underneath using a spray gun with an aqueous suspension of a wettable powder having the following composition (by weight):

- | | |
|---|-----|
| — active material to be tested | 20% |
| — deflocculant (calcium lignosulphate) | 5% |
| — wetting agent (sodium alkylaryl sulphonate) | 1% |
| — filler (aluminium silicate) | 74% |

in the required dilution containing the active material to be tested in the required dose. Each test was repeated three times.

After 48 hours, the plants were contaminated by spraying the leaves underneath with an aqueous suspension of approximately 80,000 units/cc of spores of the fungus.

The pots were then placed in an incubation cell at 20° C/100% relative humidity for a period of 48 hours.

The plants were inspected 9 days under infestation.

Under these conditions, it was found that, in a dose of 0.5 g/l, compounds 1 to 8, 10, 12, 13, 14, 16, 17, 19, 20 and 24 afford total protection, whilst compounds 15, 18, 21, 22, 25, 26, 27 afford good protection.

In addition, it was found that none of the compounds tested showed the least phytotoxicity.

b) *Treatment after contamination*

The procedure was as described in a) above, except that the plants were first

of all contaminated and then treated with the active material to be tested, the plants being inspected 9 days after contamination.

Under these conditions, it was found that, in a dose of 1 g/l, compounds 1 to 8, 14, 16, 17, 21, 22, 24, 25 and 26, completely stop the development of mildew on the vine plants.

c) *Systemic test by root absorption on vine mildew*

Several vine stocks (Gamay variety) each accommodated in a pot containing vermiculite and a nutritive solution were sprinkled with a solution containing 0.5 g/l of the material to be tested. After 2 days, the vine was contaminated with an aqueous suspension containing 100,000 spores/cc of *Plasmopara viticola*. The spores were then left to incubate for 48 hours in a room at 20° C/100% relative humidity. The degree of infestation is assessed after about 9 days in relation to an infested control which had been sprinkled with 40 cc of distilled water.

Under these conditions, it was found that, in this dose of 0.5 g/l, compounds 1 to 8, 12, 17, 19, 21, 22, 25, absorbed by the roots afford total protection, whilst compounds 10, 13, and 23 afford good protection to the vine leaves against mildew, which clearly demonstrates the systemic nature of these compounds.

d) *Open-air test*

Groups of vine stocks (Gamay variety) are treated on the 27th June, 14th, 11th and 18th July, 1st and 7th August, with a spray of wettable powder containing 50% of an active material, namely compound 13 or with maneb i.e. manganese ethylene-1,2-bis-dithiocarbamate.

The following Table shows the results of inspections made approximately 1 month, 2 months and 2.5 months after the last treatment. It should be noted that, in August and September, the mildew *Plasmopara viticola* was extremely virulent on account of heavy rainfall. For a uniform dose of 2 g/l, the results are expressed as percentage protection in relation to a contaminated but untreated control.

Compound	Inspection date		
	3/9	2/10	20/10
No. 13	94	66	50
Maneb	96	62	15
Control	15	0	0

This Table clearly shows the remarkable persistence of the composition according to the invention. In addition, no evidence of phytotoxicity was found in any of the treated plants.

These Examples clearly demonstrate the remarkable fungicidal properties of the compositions according to the invention. Individually they are characterised by their immediate, persistent or systemic effect, in particular upon vine mildew.

Some of these compounds, more 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.

EXAMPLE 3: Avocado test.

Avocado seedlings (variety *Persea indica*) were planted in a soil infested with *Phytophthora cinnamomi*, after which the soil was sprayed with a solution containing 3 g/l of ammonium phosphite. Some seedlings were left untreated as controls. Under these conditions, it was found after 20 days that the roots of the controls were completely dead, whilst 90% of the treated seedlings were healthy.

EXAMPLE 4: Pineapple test.

Pineapple seedlings were contaminated with *Phytophthora parasitica* and then treated after 48 hours by spraying with a solution containing 0.5 g/l of calcium phosphite. After 30 days, the fungus was completely inhibited in the treated seedlings, whilst the controls were infested.

All these Examples clearly show the remarkable fungicidal activity of the compounds according to the invention, on the one hand a systemic anti-mildew activity which both prevents and stops the development of the vine mildew, and on the other hand on certain phytophthora as well.

However, they have also been found to be extremely effective in controlling other types of parasitic fungi such as *Peronospora tabacci*, *Pseudoperonospora humili*, *Phytophthora cactorum*, *Phytophthora capsici*, *Bremia lactucae*, *Phytophthora infestans*, *Peronospora sp.*, *Phytophthora palmivora*, *Phytophthora phaseoli*, *Phytophthora megasperma*, *Phytophthora drechsteri* and other *Phytophthora sp.*, in other temperate-climate or tropical-climate plants such as: tobacco, hop, market-gardening cultures, especially strawberry plants, green pepper, onion, sweet pepper, tomato, bean, and in ornamental plants, in pineapple, soya, citrus, cocoa, coconut palm, hevea rubber. Accordingly, the compositions according to the invention are particularly suitable for use in the preventive or curative treatment of fungus disease in plants, especially fungus disease caused by phycomycetes in the vegetables already mentioned, but also in other plants which can be attacked by these fungi.

The compositions according to the invention may be used with advantage in admixture with one another or with other known fungicides, such as metal dithiocarbamates (maneb, zineb, mancozeb), basic salts or hydroxides of copper (oxychloride, oxysulphate), (tetrahydro) phthalimides (captan, captafol, folpel), N-(1-butyl carbamoyl)-2-benzimidazole, methyl carbamate (benomyl), 1,2-di-(3-methoxy or ethoxy)-carbonyl-2-thioureidobenzenes (thiophanates) and methyl 2-benzimidazole carbamate, either to complete the range of activity of the compositions according to the invention or to increase their persistence.

It has also been found that the compositions according to the invention may be mixed with other fungicidal, anti-mildew phosphorus derivatives, especially those to which the French Patent Application 73 43081 relates, and the 2-hydroxy-1,3,2-dioxaphospholanes, the β -hydroxyethyl phosphites, the phosphonic monoesters and their salts, the phosphonic diesters, the cyclic diphosphorus compounds and the aminophosphites disclosed, respectively, in French Patent Applications Nos. 73 01803, 73 37994, 73 45627, 71 08995, 74 10988 and 74 13246.

The doses in which the compositions according to the invention are used may vary within wide limits, depending both upon the virulence of the fungus and upon the climatic conditions. Doses of from 0.01 to 5 g/l of active material are generally suitable.

For their practical application, the active ingredients of the compositions according to the invention may be used on their own but most preferably they form part of formulations which, as a rule, contain a carrier or diluent and/or a surfactant in addition to the active material according to the invention.

In the context of the invention, a carrier or diluent includes an organic or mineral, natural or synthetic material with which the active material is associated to facilitate its application to the plant, to seeds or to soil, or its transportation or handling. The carrier or diluent can be solid (clays, natural or synthetic, silicates, resins, waxes, solid fertilisers) or fluid (water, alcohols, ketones, petroleum fractions, chlorinated hydrocarbons, liquefied gases).

The surfactant can be an ionic or non-ionic emulsifier, dispersant or wetting agent such as, for example, salts of polyacrylic acids and lignin-sulphonic acids, condensates of ethylene oxide with fatty alcohols, fatty acids or fatty amines.

The compositions according to the invention can be prepared in the form of wettable powders, soluble powders dusting powders, granulates, solutions, emulsifiable concentrates, emulsions, suspended concentrates and aerosols.

The wettable powders according to the invention can be prepared in such a way that they contain from 200 to 95% by weight of the active ingredient and they normally contain, in addition to a solid carrier, from 0 to 5% by weight of a wetting agent, from 3 to 10% by weight of a dispersant and, when necessary, from 0 to 10% by weight of one or more stabilisers and/or other additives, such as penetration agents, adhesives or anti-lumping agents, colorants etc.

Example of a Composition

One example of the composition of a wettable powder is given below:

— active material	50%
— calcium lignosulphate (deflocculant)	5%
— anionic wetting agent	1%
— antilumping silica	5%
— kaolin (filler)	39%

Powders soluble in water may be obtained by mixing from 20 to 95% by weight of the active ingredient, from 0 to 10% by weight of an anti lumping agent, the remainder being a hydrosoluble filler, mainly a salt.

Example of a Composition of a soluble powder

— active material	70%
— anionic wetting agent	0.5%
— antilumping silica	5.0%
— sodium sulphate	24.5%

Aqueous dispersions and emulsions, for example 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 invention. These emulsions can be of the water-in-oil type or of the oil-in-water type, and can have a thick consistency resembling that of a "mayonnaise".

The compositions according to the invention can contain other ingredients, for example protective colloids, adhesives or thickeners, thixotropic agents, stabilisers or sequestrants, as well as other active materials known to have pesticidal properties, especially acaricides or insecticides.

The compositions thus defined may be applied to the plants to be protected by conventional methods of applying pesticides, such as spraying, scattering, powdering, soaking.

WHAT WE CLAIM IS:—

1. A fungicidal composition comprising as active ingredient a compound containing the phosphite anion together with a carrier or diluent therefor.

2. A fungicidal composition as claimed in claim 1, wherein the active ingredient is a phosphorus acid or a mineral or organic salt of phosphorous acid.

3. A fungicidal composition as claimed in claim 1, wherein the active ingredient is an acid phosphite.

4. A fungicidal composition as claimed in claim 1, wherein the active ingredient is a neutral phosphite.

5. A fungicidal composition as claimed in any of claims 1 to 4, wherein the active ingredient is a metallic phosphite.

6. A fungicidal composition as claimed in any of claims 1 to 4 wherein the active ingredient is a nitrogenation phosphite.

7. A fungicidal composition as claimed in claim 5, wherein the metal is sodium.

8. A fungicidal composition as claimed in claim 1, wherein the active ingredient is an acid sodium phosphite.

9. A fungicidal composition as claimed in claim 1, wherein the active ingredient is a calcium phosphite.

10. A fungicidal composition as claimed in claim 5, wherein the metal is copper.

11. A fungicidal composition as claimed in claim 1, wherein the active ingredient is neutral copper phosphite.

12. A fungicidal composition as claimed in claim 1, wherein the active ingredient is an aluminium phosphite.

13. A fungicidal composition as claimed in claim 1, wherein the active ingredient is acid ammonium phosphite.

14. A fungicidal composition as claimed in claim 6, wherein the nitrogen-containing phosphite is an imidazole, cyclohexylamine, optionally substituted aniline or morpholine salt.

15. A fungicidal composition as claimed in claim 4, wherein the active ingredient is an aniline salt substituted by 1 to 3 alkyl radicals containing from 1 to 4 carbon atoms.



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Example of a Composition

One example of the composition of a wettable powder is given below:

—	active material	50%	
5	— calcium lignosulphate (deflocculant)	5%	
	— anionic wetting agent	1%	5
	— antilumping silica	5%	
	— kaolin (filler)	39%	

10 Powders soluble in water may be obtained by mixing from 20 to 95% by weight of the active ingredient, from 0 to 10% by weight of an anti lumping agent, the remainder being a hydrosoluble filler, mainly a salt. 10

Example of a Composition of a soluble powder

—	active material	70%	
15	— anionic wetting agent	0.5%	
	— antilumping silica	5.0%	
	— sodium sulphate	24.5%	15

20 Aqueous dispersions and emulsions, for example 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 invention. These emulsions can be of the water-in-oil type or of the oil-in-water type, and can have a thick consistency resembling that of a "mayonnaise". 20

25 The compositions according to the invention can contain other ingredients, for example protective colliods, adhesives or thickeners, thixotropic agents, stabilisers or sequestrants, as well as other active materials known to have pesticidal properties, especially acaricides or insecticides. 25

The compositions thus defined may be applied to the plants to be protected by conventional methods of applying pesticides, such as spraying, scattering, powdering, soaking.

WHAT WE CLAIM IS:—

- 30 1. A fungicidal composition comprising as active ingredient a compound containing the phosphite anion together with a carrier or diluent therefor. 30
2. A fungicidal composition as claimed in claim 1, wherein the active ingredient is a phosphorus acid or a mineral or organic salt of phosphorous acid.
3. A fungicidal composition as claimed in claim 1, wherein the active ingredient is an acid phosphite.
- 35 4. A fungicidal composition as claimed in claim 1, wherein the active ingredient is a neutral phosphite. 35
5. A fungicidal composition as claimed in any of claims 1 to 4, wherein the active ingredient is a metallic phosphite.
6. A fungicidal composition as claimed in any of claims 1 to 4 wherein the active ingredient is a nitrogencation phosphite.
- 40 7. A fungicidal composition as claimed in claim 5, wherein the metal is sodium. 40
8. A fungicidal composition as claimed in claim 1, wherein the active ingredient is an acid sodium phosphite.
9. A fungicidal composition as claimed in claim 1, wherein the active ingredient is a calcium phosphite.
- 45 10. A fungicidal composition as claimed in claim 5, wherein the metal is copper. 45
11. A fungicidal composition as claimed in claim 1, wherein the active ingredient is neutral copper phosphite.
12. A fungicidal composition as claimed in claim 1, wherein the active ingredient is an aluminium phosphite.
- 50 13. A fungicidal composition as claimed in claim 1, wherein the active ingredient is acid ammonium phosphite. 50
14. A fungicidal composition as claimed in claim 6, wherein the nitrogen-containing phosphite is an imidazole, cyclohexylamine, optionally substituted aniline or morpholine salt.
- 55 15. A fungicidal composition as claimed in claim 4, wherein the active ingredient is an aniline salt substituted by 1 to 3 alkyl radicals containing from 1 to 4 carbon atoms. 55

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16. A fungicidal composition as claimed in claim 1, wherein the active ingredient is a mixture of a water soluble phosphite and a substantially water-insoluble metal phosphite.

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17. A fungicidal composition as claimed in any of claims 1 to 16 which also comprises a surfactant.

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18. A fungicidal composition as claimed in claim 1, substantially as herein described with reference to any of the specific Examples.

19. A method of preventing or combatting a fungus disease which, comprises applying to the fungus or to its environment a compound containing the phosphite anion.

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20. A method of preventing or combatting a fungus disease which comprises applying to the fungus or to its environment a composition as claimed in any of claims 1 to 18.

21. A method as claimed in claim 19 to 20 for curing or preventing fungus disease in plants.

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22. A method as claimed in claim 21 wherein the compound containing the phosphite anion or the composition is applied to plants for the treatment of vine mildew.

23. A method for preventing or combatting fungus disease substantially as herein described with reference to any of the specific Examples.

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24. Plants treated by the method claimed in any of claims 21 to 23.

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