

PATENT SPECIFICATION

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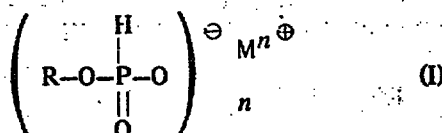
(54) FUNGICIDES

(71) We, PHILAGRO, formerly known as Pepro 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 fungicides.

In particular, this invention relates to fungicidal compositions based on monoesters of phosphonic acid (or phosphonates) and their salts. These compounds are sometimes also referred to as monoalkyl (aryl . . .) phosphites.

The invention provides a fungicidal composition suitable for use in controlling parasitic fungi in plants which contain in conjunction with an inert support and, in the case when the support is a liquid, together with a surfactant an active material comprising at least one compound corresponding to the general formula (I):



in which

R is a linear or branched chain alkyl radical containing from 1 to 18 carbon atoms and preferably from 1 to 8 carbon atoms which is unsubstituted or substituted by halogen or nitro; an alkenyl or alkynyl radical, an alkoxy alkyl radical or an alkenoxy alkyl radical, each of which is unsubstituted or substituted by halogen and the hydrocarbon portion of these four types of radicals containing from 1 to 8 and preferably from 1 to 5 carbon atoms, a cyclohexyl radical, an optionally substituted aryl radical, preferably phenyl, or aryl alkyl radical, preferably phenyl alkyl, or a heterocyclic radical optionally attached to the oxygen through an aliphatic chain, preferably tetrahydrofuryl,

M represents a hydrogen atom, an ammonium cation, ammonium substituted by 1 to 4 alkyl or hydroxy alkyl radicals containing from 1 to 5 carbon atoms or by 1 to 2 cyclohexyl radicals or a phenyl radical, or a cation of a metal from the group comprising the alkali metals, preferably sodium and potassium, alkaline earth metals, preferably magnesium, barium, calcium, and polyvalent metals such as, preferably, zinc, manganese copper (II) and (III), iron, nickel, aluminium,

n is an integer equal to the valency of M.

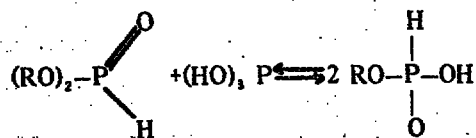
Some of these compounds are known *per se*. V. V. Orlovski et al, Journal of Gen. Chem. USSR, Vol. 42, p. 1924 (1972) describe the preparation of numerous salts of monoalkyl phosphites and, in particular, monoethyl phosphites with metallic or ammon-

ium cations substituted to a greater or lesser extent, although they do not mention the fact that these compounds have fungicidal properties.

It has now been found that these compounds I show excellent fungicidal properties, especially with respect to various types of mildew, such as mildew of the vine, tobacco mildew and hop mildew.

These compounds may be obtained by the following general methods (*cf.* Houben-Weyl, Vol. XII/2).

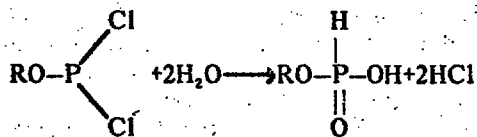
First of all, phosphonates may be prepared by transesterifying a dialkyl phosphonate with phosphorous acid (E. E. NIFANTEV, L. P. LEVITAN, C.A. 1107e 1966) in accordance with the following scheme:



O-ethyl phosphonate was prepared by this process: an equimolecular mixture of O,O-diethyl phosphonate and phosphorous acid was heated for 6 hours to 150° C. A liquid of index $n_D^{20}=1.4211$ and of density $d=1.0043$ (20° C.) was obtained in a quantitative yield.

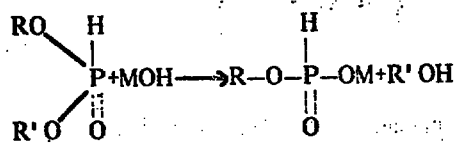
The following compounds may also be prepared by this method: O-methyl phosphonate, O-n-hexyl phosphonate, O-iso-octyl phosphonate, O-n-nonyl phosphonate, O-n-decyl phosphonate, O-n-dodecyl phosphonate, O-n-hexadecyl phosphonate, O-cyclohexyl phosphonate, O-phenyl phosphonate and O-benzyl phosphonate.

It is also possible to obtain (*cf.* Houben-Weyl, Vol. XII/2, page 6) esters according to the invention by hydrolysing a phosphorous acid dichloride with two equivalents of water in accordance with the following scheme:



O-octyl phosphonate in particular may be prepared by this method.

So far as the salts are concerned, they may be prepared by at least two methods: the first (*cf.* Houben-Weyl, Vol. XII, page 7) comprises hydrolysing or saponifying an O,O-dialkyl phosphonate in accordance with the following scheme:



This method is particularly suitable for alkali metal salts and ammonium salts.

I—Alkali metal and ammonium salts

Saponification is carried out with a mineral or organic base in aqueous solution. The reaction takes place in 1 to 4 hours at a temperature ranging from ambient temperature to the reflux temperature (aqueous medium). The products obtained, which are liquids or solids generally soluble in water, are separated by eliminating the water and the solvent, if any.

Sodium O-ethyl phosphonate was prepared in this way. One equivalent of soda in hydroalcoholic solution was added dropwise with stirring to a hydroalcoholic solution of O,O-diethyl phosphonate. After standing for 2 hours, the alcohol and water were removed by distillation under reduced pressure in a water bath. The solid residue was recrystallised from absolute alcohol.

Melting point: >300° C., yield: 68%.

Analysis for $C_2H_5O_3Na$ P

%	C	H	P
Calculated	18.18	4.54	23.45
Found	18.18	4.63	23.38

The following salts were prepared by this method:

- | | | | |
|----|--|------------------|----|
| 5 | — sodium O-methyl phosphonate: | m.p. 125° C. | 5 |
| | — sodium O- <i>n</i> -propyl phosphonate: | m.p. 195—196° C. | |
| | — sodium O-isopropyl phosphonate: | m.p. 132—133° C. | |
| | — sodium O- <i>n</i> -butyl phosphonate: | m.p. 178° C. | |
| | — sodium O- <i>n</i> -octyl phosphonate: | m.p. 167° C. | |
| 10 | — sodium O- <i>n</i> -dodecyl phosphonate: | m.p. 100° C. | 10 |
| | — sodium O- <i>n</i> -hexadecyl phosphonate: | m.p. 52° C. | |

The ammonium salts were obtained in the following manner illustrated for ammonium O-ethyl phosphonate:

0.036 mole of O,O-diethyl phosphonate was dissolved in a 25% aqueous ammonia solution. After standing for 1 hour, the solution was evaporated under reduced pressure in a water bath. The initially rubbery and colourless residue crystallised. Crystals in the form of colourless needles were obtained by crystallisation in a mixture of ethanol and acetone.

Yield: 87%, m.p.: 99–100° C.

20	Analysis for $C_2H_{10}NO_3P$				20
	%	C	H	N	P
	Calculated	18.90	7.87	11.02	24.41
	Found	18.93	7.90	11.10	24.29

25 Other alkali metal salts, whose characteristics and, where necessary, the particular preparation conditions are shown in the following Table, were obtained by changing the saponification base and/or the alkyl radical in the procedure described above: 25

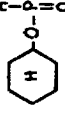
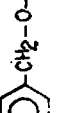
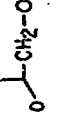
$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \text{M}^{\oplus} \\ \\ \text{O} \end{array}$					
R	M [⊕]	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Centesimal analysis found
CH ₃ -CH ₂ -CH- CH ₃	Na	C ₄ H ₁₀ NaO ₃ P	white hygroscopic, soluble solid	C 30.00 H 6.25 Na 14.38 P 19.38	29.84 6.29 14.29 19.22
CH ₃ -CH-CH ₃ CH ₃	Na	C ₄ H ₁₀ NaO ₃ P	white hygroscopic, soluble solid	C 30.00 H 6.25 Na 14.38 P 19.38	29.84 6.30 14.13 19.37
CH ₃ O-CH ₂ -CH ₂ -	Na	C ₃ H ₈ NaO ₄ P	white hygroscopic, soluble solid	C 22.22 H 4.94 Na 14.20 P 19.14	22.16 5.05 14.16 19.20
CH ₃ -CH ₂ -	K	C ₂ H ₅ KO ₃ P	m.p.: 139°C soluble	C 16.4 H 4.05 K 26.4 P 20.9	16.3 4.11 26.31 20.86
					Reaction with potash in hydroalcoholic solution at 45°C

Chemical structure	Empirical formula	Physical constants	Yield	Centesimal analysis % Calculated Found
$\text{R}-\text{O}-\text{P}(\text{O})(\text{H})\text{O}^{\ominus}\text{NH}_4^{\oplus}$				
$\text{CH}_3\text{O}-\text{P}(\text{O})(\text{H})\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{CH}_4\text{NO}_3\text{P}$	hygroscopic product	79%	C 10.62 10.76 H 7.08 7.02 N 12.39 12.37 P 27.43 27.30
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{O}-\text{P}(\text{O})(\text{H})\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_3\text{H}_{12}\text{NO}_3\text{P}$	hygroscopic product	100%	C 25.53 25.76 H 8.51 8.66 N 9.93 9.93 P 21.99 21.67
$\text{CH}_3-\text{CH}(\text{CH}_3)-\text{O}-\text{P}(\text{O})(\text{H})\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_3\text{H}_{12}\text{NO}_3\text{P}$	hygroscopic product m.p.: 131°C	31%	C 25.53 25.71 H 8.51 8.76 N 9.93 9.98 P 21.99 21.96
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{P}(\text{O})(\text{H})\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_4\text{H}_{14}\text{NO}_3\text{P}$	hygroscopic product	81%	C 30.97 30.94 H 9.03 9.03 N 9.03 8.94 P 20.00 20.10
$\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-\text{P}(\text{O})(\text{H})\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_4\text{H}_{14}\text{NO}_3\text{P}$	m.p.: 177.5°C	99%	C 30.97 30.97 H 9.03 9.17 N 9.03 8.96 P 20.00 19.94

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Chemical structure	Empirical formula	Physical constants	Yield	Centesimal analysis % Calculated	Centesimal analysis Found
$\text{R}-\text{O}-\text{P}(\text{H})(\text{O})-\text{O}^{\ominus}\text{NH}_4^{\oplus}$					
$\text{CH}_3-\text{C}(\text{H})(\text{O})-\text{P}(\text{H})(\text{O})-\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_4\text{H}_9\text{NO}_3\text{P}$	m.p. 164.5°	62%	C 31.00 H 9.03 N 9.03 P 20.00	31.04 9.05 9.18 20.13
$n\text{C}_4\text{H}_9-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{O}-\text{P}(\text{H})(\text{O})-\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_9\text{H}_{22}\text{NO}_3\text{P}$	—	82%	C 45.50 H 10.43 N 6.64 P 14.69	44.25 10.08 6.79 15.10
$\text{CH}_3-(\text{CH}_2)_5-\text{O}-\text{P}(\text{H})(\text{O})-\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_8\text{H}_{18}\text{NO}_3\text{P}$	—	34%	C 39.30 H 9.85 N 7.65 P 16.92	37.19 9.80 7.78 17.89
$\text{ClCH}_2-\text{CH}_2-\text{O}-\text{P}(\text{H})(\text{O})-\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_2\text{H}_5\text{ClNO}_3\text{P}$		62%	C 14.87 H 5.57 N 8.67 P 19.20	14.78 5.69 8.70 19.19
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{P}(\text{H})(\text{O})-\text{O}^{\ominus}\text{NH}_4^{\oplus}$	$\text{C}_3\text{H}_9\text{NO}_4\text{P}$	m.p. 56.5°	79%	C 22.93 H 7.65 N 8.92 P 19.75	22.87 7.65 8.89 19.90

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$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{P}-\text{O}^{\ominus}\text{M}^{\oplus} \\ \\ \text{O} \end{array}$	Empirical formula	Physical constants	Yield	Centesimal analysis % Calculated Found
$\begin{array}{c} \text{H} \\ \\ \text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{P}-\text{O}^{\ominus}\text{NH}_4^{\oplus} \\ \\ \text{O} \end{array}$	$\text{C}_3\text{H}_5\text{NO}_3\text{P}$	hygroscopic product	80%	C 25.90 25.83 H 7.19 7.30 N 10.07 10.10 P 22.30 22.22
$\begin{array}{c} \text{H} \\ \\ \text{CH}-\text{C}-\text{CH}_2-\text{O}-\text{P}-\text{O}^{\ominus}\text{NH}_4^{\oplus} \\ \\ \text{O} \end{array}$	$\text{C}_3\text{H}_6\text{NO}_3\text{P}$	m.p. 69°C soluble	74%	C 26.20 26.26 H 5.84 5.84 N 10.20 10.24 P 22.60 22.53
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{P}-\text{O}^{\ominus}\text{NH}_4^{\oplus} \\ \\ \text{O} \end{array}$ 	$\text{C}_6\text{H}_{10}\text{NO}_3\text{P}$	m.p. 204°C	100%	C 39.78 39.79 H 8.84 9.14 N 7.74 7.61 P 17.13 17.20
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{P}-\text{O}^{\ominus}\text{NH}_4^{\oplus} \\ \\ \text{O} \end{array}$ 	$\text{C}_6\text{H}_9\text{NO}_3\text{P}$	m.p. 148°C soluble	90%	C 41.0 41.19 H 5.7 5.78 N 17.7 17.69 P 8.0 8.09
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{P}-\text{O}^{\ominus}\text{NH}_4^{\oplus} \\ \\ \text{O} \end{array}$ 	$\text{C}_7\text{H}_{11}\text{NO}_3\text{P}$	m.p. 153°C	41%	C 44.4 44.48 H 6.3 6.39 N 7.4 7.46 P 16.4 16.51
$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{P}-\text{O}^{\ominus}\text{NH}_4^{\oplus} \\ \\ \text{O} \end{array}$ 	$\text{C}_8\text{H}_{10}\text{NO}_3\text{P}$	m.p. 94°C	78%	C 32.80 33.29 H 7.65 7.86 N 7.65 7.26 P 16.92 15.39

II—Substituted ammonium salts

a) Alkanol amine and alkyl amine salts

Preparation of monoethanol ammonium O-ethyl phosphonate

0.05 mole of O,O-diethyl phosphite was poured into an aqueous solution of one equivalent of monoethanolamine. The reaction was carried out for 1 hour at 50° C.

Removal of the water by evaporation left a water-soluble oil.

Yield: 35%, n_D^{20} : 1.4595

Analysis for $C_4H_{11}NO_4P$

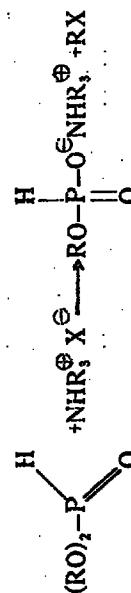
	%	C	H	N	P
Calculated		28.1	8.2	8.2	18.1
Found		28.16	8.2	8.1	18.22

Similar compounds, whose characteristics are shown in the following Table, were prepared by the same process. The yields are in excess of 85% in every case.

$ \begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \\ \\ \text{O} \\ \\ \text{N}^{\oplus}- \\ \end{array} $					
R	$\begin{array}{c} \text{N}^{\oplus} \\ \\ \text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2 \end{array}$	Empirical formula	Physical characteristics	Centesimal analysis % calculated found	Remarks
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \\ \\ \text{CH}_3 \end{array}$	$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$	$\text{C}_3\text{H}_{16}\text{NO}_5\text{P}$	oil $n_D^{20}=1.4535$ soluble	C 32.4 H 8.65 N 7.56 P 16.75 32.20 9.16 7.44 16.56	heating under reflux for 30 mins in acetonitrile
CH_3-CH_2-	$\text{H}_2\text{N}(\text{CH}_2-\text{CH}_2\text{OH})_2$	$\text{C}_4\text{H}_{18}\text{NO}_5\text{P}$	oil $n_D^{20}=1.4715$	C 33.5 H 8.38 N 6.83 P 14.4 33.23 8.29 6.70 14.27	heating under reflux for 30 mins in water
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \\ \\ \text{CH}_3 \end{array}$	$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$	$\text{C}_5\text{H}_{20}\text{NO}_5\text{P}$	oil $n_D^{20}=1.4675$ soluble	C 36.7 H 8.74 N 6.12 P 13.5 34.16 9.03 5.63 12.39	heating under reflux for 1.5 hours in water
CH_3CH_2-	$\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_3$	$\text{C}_5\text{H}_{22}\text{NO}_5\text{P}$	m.p.: 50°C soluble	C 37.1 H 8.5 N 5.4 P 11.95 37.19 8.30 5.3 12.16	heating under reflux for 1 hour in water
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \\ \\ \text{CH}_3 \end{array}$	$\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_3$	$\text{C}_6\text{H}_{24}\text{NO}_5\text{P}$	m.p.: 40°C	C 39.58 H 8.8 N 5.12 P 11.3 39.81 8.98 5.30 11.11	heating under reflux for 1.5 hours in water

$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \quad ^{\oplus} \\ \quad \\ \text{O} \quad \text{N}- \\ \\ \text{---} \end{array}$					
R	$\begin{array}{c} ^{\oplus} \\ \text{---N---} \\ \\ \text{---} \end{array}$	Empirical formula	Physical characteristics	Centesimal analysis % calculated found	Remarks
C_2H_5-	$\text{H}_3\text{N}-\text{C}_6\text{H}_5$	$\text{C}_8\text{H}_{14}\text{NO}_3\text{P}$	m.p.: 62°C soluble	C 43.7 47.26 H 6.9 7.05 N 6.9 6.96 P 15.3 15.32	heating under reflux for 30 mins in water recrystallisation from acetone
isoC_3H_7-	$\text{H}_3\text{N}-\text{C}_6\text{H}_5$	$\text{C}_9\text{H}_{16}\text{NO}_3\text{P}$	m.p.: 88°C soluble	C 49.7 49.9 H 7.36 7.06 N 6.45 6.36 P 14.30 14.36	heating under reflux for 4 hours in water recrystallisation from toluene
CH_3-CH_2-	$\text{NH}_2(\text{CH}_3)_2$	$\text{C}_4\text{H}_{14}\text{NO}_3\text{P}$	oil n_D^{20} 1.4295 soluble	C 34.58 34.58 H 10.08 10.1 N 10.08 10.06 P 22.3 21.95	heating to 60°C for 1 hour

Another method of preparing alkyl ammonium salts comprises reacting an ammonium halide with a dialkyl phosphite in accordance with the following scheme:



5 (cf. Orlovskii et al, J. Organ. Chem. USSR, 1972, Vol. 42, pages 1924-27).
The following compounds were prepared by this method:

- monoethyl ammonium O-ethyl phosphonate
- diethyl ammonium O-ethyl phosphonate
- triethyl ammonium O-ethyl phosphonate

— monoethyl ammonium O-ethyl phosphonate
 — diethyl ammonium O-ethyl phosphonate
 — triethyl ammonium O-ethyl phosphonate

b) Quaternary ammonium salts

Preparation of tetramethyl ammonium O-methyl phosphonate

0.05 mole of O,O-dimethyl phosphite was added to an equivalent quantity of trimethyl amine in solution in acetone. The reaction medium was kept at 50 to 60° C. for 2 hours. Evaporation of the acetone left a highly hygroscopic water-soluble solid.

Yield: 77%

Analysis for $C_5H_{16}NO_3P$

%	C	H	N	P
Calculated	35.5	9.47	8.28	18.35
Found	35.5	9.22	8.22	18.48

The corresponding O-ethyl and O-isopropyl derivatives were obtained by the same method, the O,O-dimethyl phosphite being replaced by the O-methyl-O-ethyl and the O-methyl-O-isopropyl phosphonate, respectively. The reaction was carried out at 70 to 100° C. in acetonitrile. The solids obtained were recrystallised from acetone.

Tetramethyl ammonium O-ethyl phosphonate

Yield: 94%, m.p.: 134° C.

Analysis for $C_6H_{18}NO_3P$

%	C	H	N	P
Calculated	39.4	9.84	7.65	16.95
Found	39.38	9.40	7.80	16.90

Tetramethyl ammonium O-isopropyl phosphonate

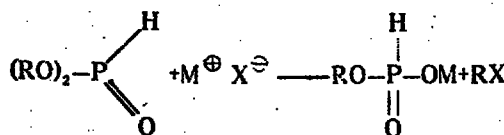
Yield: 92%, m.p.: 153° C.

Analysis for $C_7H_{20}NO_3P$

%	C	H	N	P
Calculated	42.6	10.15	7.11	15.7
Found	42.6	10.26	7.13	15.9

III—Divalent metal salts

A metal halide was reacted with a dialkyl phosphite in accordance with the following scheme:



(cf. Orlovskii et al, J. Organ. Chem. USSR, Vol. 42, pages 1924—1972).

Calcium O-ethyl phosphonate was prepared in this way.

A mixture of 11 g (0.01 mole) of calcium chloride with 2.8 g (0.02 mole) of O,O-diethyl phosphonate was heated with stirring for 2 hours to 110—130° C. The mixture was then cooled. A precipitate was obtained which, after filtration and washing, gave white crystals melting at above 420° C. in a yield of 96%.

Analysis for $C_4H_{12}O_6P_2Ca$

%	C	H
Calculated	18.6	1.5
Found	19.12	1.98

The following salts may be similarly obtained by replacing the starting salt:

- barium O-ethyl phosphonate
- zinc O-ethyl phosphonate

Magnesium O-ethyl phosphonate

0.2 mole of O,O-diethyl phosphite was added to a suspension of 0.1 mole of magnesia in 100 cc of distilled water. The exothermic reaction was carried out with

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stirring for 2 hours at 50° C. After filtration, the water was evaporated from the filtrate, leaving a white solid which was washed with acetone and then dried.

Yield: 100%, m.p.: >300° C.

Analysis for $C_4H_{12}MgO_6P_2$

5	%	C	H	Mg	P	5
	Calculated	19.83	4.96	10.02	25.63	
	Found	19.90	5.22	9.96	25.60	

10 The following Table shows the characteristics (appearance, melting point, solubility in water) and analysis of other metal alkyl phosphonates obtained in the same way as in the preceding Example. Unless otherwise indicated, the yields are in excess of 70%, the majority being quantitative. In the case of manganese salts, the metal oxide was replaced by a carbonate. 10

$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \\ \\ \text{O} \end{array} \right)_2 \text{M}^{\oplus\oplus}$					
R	M	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Remarks
$\text{CH}_3-\text{CH}_2-\text{CH}_2-$	Mg	$\text{C}_6\text{H}_{18}\text{MgO}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$	white solid m.p. > 300°C soluble	C 23.52 H 6.55 Mg 7.85 P 20.30	23.50 6.36 7.93 20.27
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \\ \\ \text{CH}_3 \end{array}$	Mg	$\text{C}_6\text{H}_{18}\text{MgO}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$	white solid m.p. = 126°C	C 26.02 H 5.92 Mg 8.9 P 22.9	26.6 5.9 9.1 22.8 analysis expressed in dry weight reaction temperature 80°C
$\text{CH}_3-(\text{CH}_2)_3-$	Mg	$\text{C}_8\text{H}_{20}\text{MgO}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$	white solid soluble	C 28.74 H 7.20 Mg 7.37 P 18.56	28.70 7.13 7.37 18.56
$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}- \\ \\ \text{CH}_3 \end{array}$	Mg	$\text{C}_8\text{H}_{20}\text{MgO}_6\text{P}_2$	white solid soluble	C 32.21 H 6.71 Mg 8.05 P 20.81	31.99 6.94 7.98 20.66
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	Mg	$\text{C}_8\text{H}_{20}\text{MgO}_6\text{P}_2 \cdot 2\text{H}_2\text{O}$	white solid soluble	C 28.74 H 7.20 Mg 7.37 P 18.56	28.63 7.16 7.29 18.70

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$$\left(\begin{array}{c} \text{H} \\ | \\ \text{R}-\text{O}-\text{P}-\text{O}^- \\ || \\ \text{O} \end{array} \right)_2 \text{M}^{++}$$

R	M	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Centesimal analysis found	Remarks
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	Mg	$\text{C}_6\text{H}_{16}\text{MgO}_6\text{P}_2$	white solid soluble	C 23.84 H 5.30 Mg 7.95 P 20.53	23.76 5.30 7.98 20.40	
$\text{CH}_3-\text{CH}_2-\text{CH}_2-$	Ca	$\text{C}_6\text{H}_{16}\text{CaO}_6\text{P}_2$	white solid soluble	C 25.17 H 5.59 Ca 13.99 P 21.68	24.96 5.90 13.74 21.56	
$\text{CH}_3-\text{CH}-\text{CH}_3$	Ca	$\text{C}_6\text{H}_{16}\text{CaO}_6\text{P}_2$	white solid m.p. > 300°C	C 25.17 H 5.59 Ca 13.99 P 21.68	25.06 6.10 13.87 21.63	Reaction temperature 60–70°C
$\text{CH}_3-(\text{CH}_2)_3-$	Ca	$\text{C}_8\text{H}_{20}\text{CaO}_6\text{P}_2$	white solid soluble	C 30.57 H 6.37 Ca 12.74 P 19.75	30.79 6.29 12.69 19.60	
$\text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3$	Ca	$\text{C}_8\text{H}_{20}\text{CaO}_6\text{P}_2$	white solid soluble	C 30.57 H 6.37 Ca 12.74 P 19.75	30.66 6.16 12.74 19.74	
$\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3$	Ca	$\text{C}_8\text{H}_{20}\text{CaO}_6\text{P}_2$	white solid soluble	C 30.57 H 6.37 Ca 12.74 P 19.75	30.60 6.43 12.90 19.59	

CH ₃			soluble	Ca 12.74 P 19.75	12.90 19.59
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$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^- \\ \\ \text{O} \end{array} \right)_2 \text{M}^{\oplus\oplus}$					
R	M	Empirical formula	Physical characteristics	Centesimal analysis, % calculated	Remarks
CH ₃ OCH ₂ CH ₂ -	Ca	C ₈ H ₁₆ CaO ₆ P ₂	white solid soluble	C 22.64 H 5.03 Ca 12.58 P 19.50	22.63 5.16 12.57 18.98
CH ₃ (CH ₂) ₃ CHCH ₂ - CH ₂ CH ₃	Ca	C ₁₆ H ₃₆ CaO ₆ P ₂ · 1, 5H ₂ O	white solid substantially insoluble	C 42.40 H 8.60 Ca 13.68 P 8.83	42.40 8.06 12.50 8.03 Yield 25%
CH ₃ -CH ₂ -	Mn	C ₄ H ₁₂ MnO ₆ P ₂	white solid m.p.=136°C soluble	C 17.6 H 4.4 Mn 20.1 P 22.7	17.4 4.3 19.9 22.7 heating under reflux
CH ₃ -CH ₂ -CH ₂ -	Mn	C ₆ H ₁₈ MnO ₆ P ₂	white solid soluble	C 23.92 H 5.31 Mn 18.27 P 20.59	23.79 5.37 18.19 20.57 heating under reflux
CH ₃ -CH- CH ₃	Mn	C ₆ H ₁₈ MnO ₆ P ₂ · 2H ₂ O	white solid soluble	C 21.59 H 5.94 Mn 16.32 P 18.40	21.50 5.60 16.50 18.32
CH ₃ (CH ₂) ₃ -	Mn	C ₈ H ₂₀ MnO ₆ P ₂	pale pink solid, soluble	C 29.17 H 6.08 Mn 16.71 P 18.94	29.56 5.76 16.79 18.80

$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \\ \\ \text{O} \end{array} \right)_2 \text{M}^{\oplus\oplus}$				
R	M	Empirical formula	Physical characteristics	Centesimal analysis % calculated found
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	Mn	$\text{C}_6\text{H}_{12}\text{O}_6\text{P}_2\text{Mn}$	pale pink solid, soluble	C 27.70 27.76 H 6.34 6.12 Mn 15.85 15.72 P 17.88 17.78 Yield 55%
$\text{CH}_3\text{CH}_2\text{CH}_2-$	Zn	$\text{C}_6\text{H}_{12}\text{O}_6\text{P}_2\text{Zn}$	highly viscous liquid, soluble	C 23.30 23.01 H 5.17 5.16 Zn 21.03 21.20 P 20.06 20.16
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \\ \\ \text{CH}_3 \end{array}$	Zn	$\text{C}_6\text{H}_{10}\text{O}_6\text{P}_2\text{Zn}$	highly viscous liquid, soluble	C 23.30 23.16 H 5.17 5.06 Zn 21.03 21.19 P 20.06 20.03

IV—Salts obtained by a double-exchange reaction

a) Synthesis via the barium salt

Zinc O-*n*-butyl phosphonate

- 5 0.05 mole of O-*n*-butyl phosphonate and 0.05 mole of baryta were dissolved in 150 cc of distilled water. The barium O-*n*-butyl phosphonate was precipitated. A solution of 0.05 mole of zinc sulphate heptahydrate in 20 cc of distilled water was then added, as a result of which the barium sulphate was precipitated. It was separated by filtration or centrifuging. The clear filtrate was evaporated to dryness, giving a highly viscous liquid which was dried *in vacuo*. This liquid was soluble in water.

Yield: 82%

Analysis for $\text{C}_6\text{H}_{10}\text{O}_6\text{P}_2\text{Zn}$

%	C	H	Zn	P
Calculated	28.31	5.89	19.17	18.28
Found	28.16	5.96	19.46	18.28

The products whose characteristics are set out in the following Table were obtained by changing either the alkyl radical or the metal in the procedure described above. Unless otherwise indicated, the yields are in excess of 70%.

61

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$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \\ \\ \text{O} \end{array} \right) \text{M}^{\text{n}\oplus} \quad \text{2 or 3}$					
R	M	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Centesimal analysis found
$\text{CH}_3\text{CH}_2\text{CH}-\text{CH}_3$	$\text{Zn}^{\oplus\oplus}$	$\text{C}_8\text{H}_{20}\text{O}_6\text{P}_2\text{Zn}$	highly viscous liquid, soluble	C 28.31 H 5.89 Zn 19.17 P 18.28	28.16 5.95 19.54 18.06
$\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3$	$\text{Zn}^{\oplus\oplus}$	$\text{C}_8\text{H}_{20}\text{O}_6\text{P}_2\text{Zn}$	highly viscous liquid, soluble	C 28.31 H 5.89 Zn 19.17 P 18.28	28.12 6.03 19.54 18.19
$\text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3$	$\text{Mn}^{\oplus\oplus}$	$\text{C}_8\text{H}_{20}\text{MnO}_6\text{P}_2$	pale pink solid, soluble	C 29.17 H 6.08 Mn 16.71 P 18.34	28.99 6.11 17.11 18.74
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	$\text{Mn}^{\oplus\oplus}$	$\text{C}_8\text{H}_{18}\text{MnO}_6\text{P}_2$	solid soluble	C H Mn P	
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	$\text{Zn}^{\oplus\oplus}$	$\text{C}_8\text{H}_{18}\text{ZnO}_6\text{P}_2$	solid soluble	C H Zn P	
$\text{CH}_3\text{OCH}_2\text{CH}_2-$	$\text{Al}^{\oplus\oplus\oplus}$	$\text{C}_9\text{H}_{24}\text{AlO}_6\text{P}_3$	solid soluble	C H Al P	

The products whose characteristics are set out in the following Table were obtained by changing either the alkyl radical or the metal in the procedure described above. Unless otherwise indicated, the yields are in excess of 70%.

63

$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \\ \\ \text{O} \end{array} \right)_2 \text{Mn}^{\oplus}$					
R	M	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Centesimal analysis found
$\text{CH}_3\text{OCH}_2\text{CH}_2$	$\text{Fe}^{\oplus\oplus}$	$\text{C}_6\text{H}_{12}\text{FeO}_6\text{P}_2$	solid soluble	C H Fe P	
CH_3CH_2	$\text{Cu}^{\oplus\oplus}$	$\text{C}_4\text{H}_{12}\text{CuO}_6\text{P}_2$	m.p. > 300°C	C 17.05 H 4.26 Cu 22.55 P 22.0	17.08 4.30 21.80 21.32

b) From the sodium salt

Aluminium O-isopropyl phosphonate

Sodium O-isopropyl phosphonate was prepared. A solution of 0.06 mole of aluminium nitrate with nine molecules of water in 30 cc of distilled water was added to a solution of 0.18 mole of compound in 150 cc of distilled water. The aluminium O-isopropyl phosphonate was precipitated. The precipitate was centrifuged, washed with water and then with acetone and finally dried *in vacuo*, giving a white solid which is insoluble in water.

Yield: 60%, m.p.: >300° C.

Analysis for $C_3H_7AlO_3P$

%	C	H	Al	P
Calculated	27.27	6.06	6.82	23.48
Found	27.19	6.28	6.90	23.50

The following compounds were prepared by the same method from analogous sodium O-alkyl phosphonate derivatives. The iron (III) salts were obtained by replacing the aluminium nitrate with ferric iron nitrate.

The characteristics of all these compounds are set out in the following Table.

Unless otherwise indicated, the yields are in excess of 70%.

65

$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^- \\ \\ \text{O} \end{array} \right)_3 \text{M}^{\oplus\oplus\oplus}$					
R	M ^{⊕⊕⊕}	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Remarks
CH ₃ -CH ₂ -CH ₂ -	Al ^{⊕⊕⊕}	C ₉ H ₁₈ AlO ₉ P ₃	white solid m.p.>300°C insoluble	C H Al P	
CH ₃ (CH ₂) ₃ -	Al ^{⊕⊕⊕}	C ₁₂ H ₂₄ AlO ₉ P ₃	white solid m.p.>300°C insoluble	C 32.88 H 6.85 Al 6.16 P 21.23	32.69 6.84 6.18 20.99
CH ₃ CH ₂ -CH- CH ₃	Al ^{⊕⊕⊕}	C ₁₂ H ₂₄ AlO ₉ P ₃	white solid m.p.>300°C insoluble	C 32.88 H 6.85 Al 6.16 P 21.23	32.76 6.98 6.19 21.19
CH ₃ -CH-CH ₂ - CH ₃	Al ^{⊕⊕⊕}	C ₁₂ H ₂₄ AlO ₉ P ₃	white solid m.p.>300°C insoluble	C 32.88 H 6.85 Al 6.16 P 21.23	32.73 6.94 6.14 21.24
CH ₃ -CH ₂ -	Al ^{⊕⊕⊕}	C ₈ H ₁₆ AlO ₉ P ₃	white solid m.p.>300°C insoluble	C 20.3 H 5.09 Al 7.6 P 26.3	20.41 5.09 7.64 26.24

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$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \\ \\ \text{O} \end{array} \right) \text{M}^{n\oplus} \quad 2 \text{ or } 3$					
R	M [⊕]	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Remarks
CH ₃ -CH ₂ -	Ni ^{⊕⊕}	C ₄ H ₁₂ NiO ₆ P ₂	m.p. > 300°C	C 17.3 H 4.3 Ni 27.10 P 22.4	15.29 4.63 21.2 17.97
CH ₃ -CH ₂ -CH ₂ -	Fe ^{⊕⊕⊕}	C ₉ H ₂₄ FeO ₉ P ₃	white solid m.p. > 300°C insoluble	C 25.41 H 5.64 Fe 13.17 P 21.88	25.36 5.92 13.16 21.88
$\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_3 \end{array}$	Fe ^{⊕⊕⊕}	C ₉ H ₂₄ FeO ₉ P ₃	white solid m.p. > 300°C insoluble	C 25.41 H 5.64 Fe 13.17 P 21.88	25.24 5.46 13.30 21.88
CH ₃ -(CH ₂) ₃ -	Fe ^{⊕⊕⊕}	C ₁₂ H ₃₀ FeO ₉ P ₃	white solid m.p. > 300°C insoluble	C 30.83 H 6.42 Fe 11.99 P 19.91	30.90 6.10 12.10 19.88

action of nickel bromide on sodium ethyl phosphonate in absolute alcohol the product contains 11% of NiBr₂

$\left(\begin{array}{c} \text{H} \\ \\ \text{R}-\text{O}-\text{P}-\text{O}^{\ominus} \\ \\ \text{O} \end{array} \right) \text{M}^{n\oplus} \quad 2 \text{ or } 3$					
R	M ^{n⊕}	Empirical formula	Physical characteristics	Centesimal analysis % calculated	Centesimal analysis found
CH ₃ -CH ₂ -CH- CH ₃	Fe ^{⊕⊕⊕}	C ₁₁ H ₃₀ FeO ₉ P ₃	white solid m.p. > 300°C insoluble	C 30.83 H 6.42 Fe 11.99 P 19.91	30.90 6.13 11.98 19.99
CH ₃ -CH-CH ₂ - CH ₃	Fe ^{⊕⊕⊕}	C ₁₂ H ₃₀ FeO ₉ P ₃	white solid m.p. > 300°C insoluble	C 30.83 H 6.42 Fe 11.99 P 19.91	30.94 6.12 12.08 20.01

V—Iron salts

Iron O-ethyl phosphonate

This compound was prepared by the method (Chem. Ber. 90, page 811) comprising reacting ferric chloride with 3 equivalents of ethyl phosphorous acid. A solid melting above 300° C. was obtained after filtration and washing.

Analysis for C₈H₁₈FeO₉P₃

%	C	H	Fe	P
Calculated	18.80	4.70	14.60	24.3
Found	18.90	3.80	14.63	24.2

Iron O-(2-chloroethyl)-phosphonate

This compound was prepared by ORLOVSKI'S method described above, replacing the soda with ferric chloride. It was possible to obtain the iron salts of the phosphonates, for example, iron O-(2-chloroethyl)-phosphonate which decomposes at around 135° C.

Analysis for C₈H₁₂Cl₂FeO₉P₃

%	C	H	N	P
Calculated	14.8	3.04	21.9	19.1
Found	14.78	3.019	21.77	18.78

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The following Examples illustrate the fungicidal properties of the following compounds:

- | | | |
|----|---|----|
| 5 | 1. Ammonium O-methyl phosphonate; | |
| | 2. Ammonium O-ethyl phosphonate; | |
| | 3. Sodium O-ethyl phosphonate; | 5 |
| | 4. Calcium O-ethyl phosphonate; | |
| | 5. Ammonium O-n-propyl phosphonate; | |
| | 6. Ammonium O-isopropyl phosphonate; | |
| 10 | 7. Ammonium O-n-butyl phosphonate; | |
| | 8. Ammonium O-n-hexyl phosphonate; | 10 |
| | 9. Ammonium O-[(2-ethyl)-n-hexyl]phosphonate; | |
| | 10. Sodium O-n-octyl phosphonate; | |
| | 11. Sodium O-n-dodecyl phosphonate; | |
| 15 | 12. Sodium O-n-hexadecyl phosphonate; | |
| | 13. Ammonium O-aliyl phosphonate; | 15 |
| | 14. Ammonium O-methoxy ethyl phosphonate; | |
| | 15. Ammonium O-cyclohexyl phosphonate; | |
| | 16. Ammonium O-benzyl phosphonate; | |
| 20 | 17. Ammonium O-tetrahydrofurfuryl phosphonate; | |
| | 18. Sodium O-methyl phosphonate; | 20 |
| | 19. Tetramethyl ammonium O-methyl phosphonate; | |
| | 20. Dicylohexyl ammonium O-methyl phosphonate; | |
| | 21. Potassium O-ethyl phosphonate; | |
| 25 | 22. Magnesium O-ethyl phosphonate; | |
| | 23. Barium O-ethyl phosphonate; | 25 |
| | 24. Zinc O-ethyl phosphonate; | |
| | 25. Manganese O-ethyl phosphonate; | |
| | 26. Aluminium O-ethyl phosphonate; | |
| 30 | 27. Iron (III) O-ethyl phosphonate; | |
| | 28. Copper (II) O-ethyl phosphonate; | 30 |
| | 29. Nickel (II) O-ethyl phosphonate; | |
| | 30. Magnesium O-n-propyl phosphonate; | |
| | 31. Sodium O-isopropyl phosphonate; | |
| 35 | 32. Calcium O-isopropyl phosphonate; | |
| | 33. Aluminium O-isopropyl phosphonate; | 35 |
| | 34. Sodium O-n-butyl phosphonate; | |
| | 35. Calcium O-n-butyl phosphonate; | |
| | 36. Ammonium O-sec.-butyl phosphonate; | |
| 40 | 37. Aluminium O-sec.-butyl phosphonate; | |
| | 38. Calcium O-n-[(2-ethyl)-n-hexyl]phosphonate; | 40 |
| | 39. Sodium O-methoxy ethyl phosphonate; | |
| | 40. Magnesium O-methoxy ethyl phosphonate; | |
| | 41. Ammonium O-propargyl phosphonate; | |
| | 42. Ammonium O-phenyl phosphonate. | |

EXAMPLE 1:

In vivo test on Plasmodiophora viticola in vine plants

a) Preventive treatment

The leaves of pot-grown vine plants (Gamay variety) were 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 alkyl aryl 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 40 cc of an aqueous suspension containing approximately 80,000 spores of the fungus per cc of the suspension.

around 150°C.
Analysis for $C_6H_{13}Cl_3FeO_3P_3$
%
Calculated
Found
C 14.8 14.78
H 3.04 3.019
N 21.9 21.77
P 19.1 18.78

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 after infestation.

5 Under these conditions, it was found that, in a dose of 0.5 g/l, compounds 1 to 9, 11 to 22, 24, 26 to 30, 32 to 38 and 40 to 42 afforded total protection, whilst compounds 23, 25, 31 and 39 afforded good protection.

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

b) *Treatment after contamination*

10 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.

15 Under these conditions, it was found that, in a dose of 1 g/l, compounds 1 to 8, 10 to 29, 31, 32, 36 and 40 to 42 completely stopped the development of mildew on the vine plants.

c) *Systemic test by root absorption*

20 Several vine stocks (Gamay variety) each accommodated in a pot containing vermiculite and a nutritive solution were sprinkled with 40 cc of 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 was assessed after about 9 days in relation to an infested control which had been sprinkled with 40 cc of distilled water.

25 Under these conditions, it was found that, in this dose of 0.5 g/l, compounds 1 to 18, 20 to 35 and 37 to 42, absorbed by the roots, afforded total protection to the vine leaves against mildew, which demonstrated clearly the systemic nature of these compounds.

EXAMPLE 2:

Open-air test on mildew of the vine

30 Groups of 5 vine stocks (Gamay variety) were sprayed every 8 days from the 5th July to the 20th August with an aqueous solution containing 200 g/hl of active material, or, in one case, a wettable powder of the following composition (by weight):

— active material (compound)	50%	
— calcium lignosulphate (deflocculant)	5%	
35 — sodium alkyl aryl sulphonate	1%	
— anti-lumping silica	5%	
— kaolin (filler)	39%	

40 The mildew (*Plasmopara viticola*) appeared from 24th July onwards. Natural contamination was considerable. In August the stocks were sprayed in such a way that the leaves were kept permanently wet. The attacks of fungus were considerable and, in September, the mildew was promoted by particularly wet weather.

At the end of October, the number of mildewed areas per plot was counted on the leaves which had been effectively treated.

45 Under these conditions, it was found that the controls showed 136 mildewed areas per plot, whereas the plots treated with compounds numbers 2, 3, 4, 21, 22, 26, 31 and 39 did not show the least sign of mildew.

In addition, the shoots which were not present during the treatments showed only a few mildewed areas per plot, which adequately confirmed the systemic character of these compounds under glass.

EXAMPLE 3:

Test on tobacco

50 Groups of 5 tobacco plants (PB 91) were treated on the 15th June with a wettable powder containing 160 g/l of manebe (80%), 300 g/l of sodium O-ethyl phosphonate and 300 g/l of magnesium O-ethyl phosphonate (50%). One group was left untreated as control.

55 After 48 hours, the plants were artificially contaminated (with *Peronospora tabacina*) and then finely sprayed with water. The treatment was then continued once weekly.

An inspection was made on the 12th August by counting the number of mildewed areas per group. The results are set out in the following Table:

Product	Number of mildewed areas per group
Control	48
Maneb	4
Sodium O-ethyl phosphonate	2
Magnesium O-ethyl phosphonate	1

Other tests show that the two compounds according to the invention are also effective against this fungus in curative treatment, and have a systemic action.

EXAMPLE 4:

Avocado test

Young avocado plants (variety *Persea indica*) were planted in soil infested with *Phytophthora cinnamomi*, after which the soil was sprayed with a solution containing 3 g/l of aluminium O-ethyl phosphonate. Some plants were left untreated as controls. Under these conditions, it was found after 20 days that the roots of the control plants were completely destroyed, whilst 90% of the roots of the treated plants were healthy.

EXAMPLE 5:

Pineapple test

Young pineapple plants were contaminated with *Phytophthora parasitica*, and then treated after 48 hours by spraying with a solution containing 0.5 g/l of calcium O-ethyl phosphonate. It was found after 30 days that the fungus was completely inhibited in the treated plants, whilst the controls were infested.

EXAMPLE 6:

Strawberry test

Ten strawberry plants (variety *Surprise des Halles*) were treated by soaking for 1 hour in an aqueous solution containing 0.2% of calcium O-isopropyl phosphonate, dried and then planted out, on the 14th June, in soil artificially contaminated with *Phytophthora cactorum*. Immediately afterwards and then once every 8 days until the 18th July, the plants were sprayed with the same solution which corresponded to a total application of 0.5 g of active material per plant.

Plants treated by soaking and spraying with water were used as controls.

Under these conditions, it was found on the 24th July that the protection afforded to the strawberry plants was complete, whilst 76% of the control plants were dead.

EXAMPLE 7:

Pimento test

10 pimento plants (variety *Yolo wonder*) which had already been planted out were transplanted on the 27th June to pots of earth artificially contaminated with *Phytophthora capsici*. The plants were sprayed immediately and then once every 8 days until the 18th July with an aqueous solution containing zinc O-ethyl phosphonate so as to apply a total of 0.5 g of treatment per plant.

Plants sprayed with water were used as controls.

Under these conditions, it was found that the 10 plants were intact at the end of August, whilst the control plants had all died by 25th July.

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 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 *Guignardia bidwellii* in vine, *Pseudoperonospora humuli*, *Bremia lactucae*, *Phytophthora infestans*, *Peronospora* sp., *Phytophthora palmivora*, *Phytophthora phascoli*, *Phytophthora megasperma*, *Phytophthora drechsleri* and other *Phytophthora* sp. in temperate-climate or tropical-climate plants such as tobacco,

market-gardening cultures, especially onion, sweet pepper, tomato, bean, in ornamental plants, in 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* and *ascomycetes* in the vegetables already mentioned, but also more generally in agriculture, arboriculture, horticulture, market gardening, but more especially in viticulture.

The compounds I 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 (ceptane, captafol, folpet), N-(1-butyl carbamoyl)-2-benzimidazole, methyl carbamate (benomyl), 1,2-di-(3-methoxy or ethoxy)-carbonyl-2-thioureido benzenes (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 compounds according to the invention may be mixed with other fungicidal, anti-mildew phosphorus derivatives, especially 2-hydroxy-1,3,2-dioxaphospholanes, β -hydroxy ethyl phosphites and phosphorous acid and its salts.

The doses in which the compounds 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 compounds according to the invention are rarely used on their own. Instead, they generally form part of formulations which, as a rule, contain a support and/or a surfactant in addition to the active material according to the invention.

In the context of the invention, a support is 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 support can be solid (e.g. clays, natural or synthetic silicates, resins, waxes or solid fertilisers) or liquid (e.g. water, alcohols, ketones, petroleum fractions, chlorinated hydrocarbons or liquefied gases). In the case where the support is a liquid, a surfactant is also necessarily present.

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 so that they contain from 20 to 95% by weight of the active material, and they normally contain, in addition to a solid support, 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 and colorants for example.

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 are obtained by mixing from 20 to 95% by weight of the active material, from 0 to 10% by weight of an antilumping agent, the remainder being a hydrosoluble filler mainly a salt.

There is one example of composition of a soluble powder:

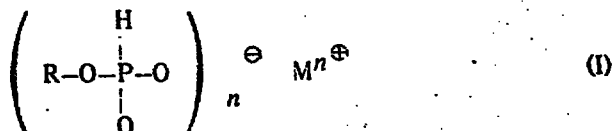
— active material	70%
— anionic wetting agent	0.5%
— antilumping silica	5%
— sodium sulphate (soluble filler)	24.5%

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.

WHAT WE CLAIM IS:—

1. A fungicidal composition which comprises as active material at least one compound corresponding to the general formula (I)



in which

R is a linear or branched chain alkyl radical containing from 1 to 18 carbon atoms which is unsubstituted or substituted by halogen or nitro; an alkenyl, alkynyl, alkoxy alkyl, or alkenoxy alkyl radical, each of which is unsubstituted or substituted by halogen and the hydrocarbon portion of each radical contains from 1 to 8 carbon atoms; a cyclohexyl radical; an optionally substituted aryl radical, or aryl alkyl radical; or a heterocyclic radical optionally attached to the oxygen atom through an aliphatic chain, preferably tetrahydrofurfuryl,

M represents a hydrogen atom, an ammonium cation, ammonium substituted by from 1 to 4 alkyl or hydroxy alkyl radicals containing from 1 to 5 carbon atoms or by 1 or 2 cyclohexyl radicals or a phenyl radical, or a cation of a metal comprising an alkali metal, an alkaline earth metal, or a polyvalent metal,

n is an integer equal to the valency of M, in conjunction with an inert support with the proviso that, when the support is a liquid, a surfactant is also present.

2. A fungicidal composition as claimed in Claim 1, wherein R is a linear or branched chain alkyl radical containing from 1 to 8 carbon atoms.

3. A fungicidal composition as claimed in Claim 1, wherein R is an alkenyl, alkynyl, alkoxy alkyl or alkenoxy alkyl radical in which the hydrocarbon portion contains from 1 to 5 carbon atoms.

4. A fungicidal composition as claimed in Claim 1, wherein R is an optionally substituted phenyl radical.

5. A fungicidal composition as claimed in Claim 1, wherein R is an optionally substituted phenyl alkyl radical.

6. A fungicidal composition as claimed in any of Claims 1 to 5, wherein M is sodium or potassium.

7. A fungicidal composition as claimed in any of Claims 1 to 5, wherein M is magnesium, barium or calcium.

8. A fungicidal composition as claimed in any of Claims 1 to 5, wherein M is a cation of a metal comprising zinc, manganese, copper (II) or copper (III), iron (II) or iron (III), nickel or aluminium.

9. A fungicidal composition as claimed in Claim 2 or 3, wherein R is an alkyl radical, a halogenated alkyl radical containing from 1 to 4 carbon atoms, an allyl, propargyl, allyl oxy or alkoxy alkyl radical containing from 2 to 3 carbon atoms.

10. A fungicidal composition as claimed in Claim 9, wherein R is the ethyl radical.

11. A fungicidal composition as claimed in Claim 9, wherein R is the isopropyl radical.

12. A fungicidal composition as claimed in Claim 10, wherein the active material is sodium O-ethyl phosphonate.

13. A fungicidal composition as claimed in Claim 10, wherein the active material is calcium O-ethyl phosphonate.

14. A fungicidal composition as claimed in Claim 10, wherein the active material is aluminium O-ethyl phosphonate.

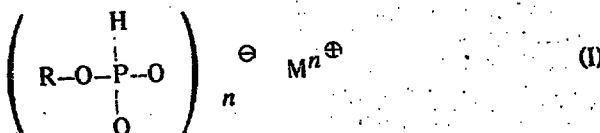


Aqueous dispersions and emulsions, for example compositions obtained by diluting with water a wettable powder or an emulsifiable concentrate according to the invention, are included within the general scope of the invention. These emulsions can be of the water-in-oil type or of the oil-in-water type, 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.

WHAT WE CLAIM IS:—

1. A fungicidal composition which comprises as active material at least one compound corresponding to the general formula (I)



in which

R is a linear or branched chain alkyl radical containing from 1 to 18 carbon atoms which is unsubstituted or substituted by halogen or nitro; an alkenyl, alkynyl, alkoxy alkyl, or alkenoxy alkyl radical, each of which is unsubstituted or substituted by halogen and the hydrocarbon portion of each radical contains from 1 to 8 carbon atoms; a cyclohexyl radical; an optionally substituted aryl radical, or aryl alkyl radical; or a heterocyclic radical optionally attached to the oxygen atom through an aliphatic chain, preferably tetrahydrofurfuryl,

M represents a hydrogen atom, an ammonium cation, ammonium substituted by from 1 to 4 alkyl or hydroxy alkyl radicals containing from 1 to 5 carbon atoms or by 1 or 2 cyclohexyl radicals or a phenyl radical, or a cation of a metal comprising an alkali metal, an alkaline earth metal, or a polyvalent metal,

n is an integer equal to the valency of M, in conjunction with an inert support with the proviso that, when the support is a liquid, a surfactant is also present.

2. A fungicidal composition as claimed in Claim 1, wherein R is a linear or branched chain alkyl radical containing from 1 to 8 carbon atoms.

3. A fungicidal composition as claimed in Claim 1, wherein R is an alkenyl, alkynyl, alkoxy alkyl or alkenoxy alkyl radical in which the hydrocarbon portion contains from 1 to 5 carbon atoms.

4. A fungicidal composition as claimed in Claim 1, wherein R is an optionally substituted phenyl radical.

5. A fungicidal composition as claimed in Claim 1, wherein R is an optionally substituted phenyl alkyl radical.

6. A fungicidal composition as claimed in any of Claims 1 to 5, wherein M is sodium or potassium.

7. A fungicidal composition as claimed in any of Claims 1 to 5, wherein M is magnesium, barium or calcium.

8. A fungicidal composition as claimed in any of Claims 1 to 5, wherein M is a cation of a metal comprising zinc, manganese, copper (II) or copper (III), iron (II) or iron (III), nickel or aluminium.

9. A fungicidal composition as claimed in Claim 2 or 3, wherein R is an alkyl radical, a halogenated alkyl radical containing from 1 to 4 carbon atoms, an allyl, propargyl, allyl oxy or alkoxy alkyl radical containing from 2 to 3 carbon atoms.

10. A fungicidal composition as claimed in Claim 9, wherein R is the ethyl radical.

11. A fungicidal composition as claimed in Claim 9, wherein R is the isopropyl radical.

12. A fungicidal composition as claimed in Claim 10, wherein the active material is sodium O-ethyl phosphonate.

13. A fungicidal composition as claimed in Claim 10, wherein the active material is calcium O-ethyl phosphonate.

14. A fungicidal composition as claimed in Claim 10, wherein the active material is aluminium O-ethyl phosphonate.



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15. A fungicidal composition as claimed in Claim 10, wherein the active material is magnesium O-ethyl phosphonate.
16. A fungicidal composition as claimed in Claim 10, wherein the active material is zinc O-ethyl phosphonate.
- 5 17. A fungicidal composition as claimed in Claim 10, wherein the active material is cuprous O-ethyl phosphonate.
18. A fungicidal composition as claimed in Claim 10, wherein the active material is cupric O-ethyl phosphonate.
- 10 19. A fungicidal composition as claimed in Claim 11, wherein the active material is sodium O-isopropyl phosphonate.
20. A fungicidal composition as claimed in Claim 11, wherein the active material is calcium O-isopropyl phosphonate.
21. A fungicidal composition as claimed in Claim 11, wherein the active material is aluminium O-isopropyl phosphonate.
- 15 22. A fungicidal composition as claimed in Claim 11, wherein the active material is magnesium O-isopropyl phosphonate.
23. A fungicidal composition as claimed in Claim 11, wherein the active material is zinc O-isopropyl phosphonate.
- 20 24. A fungicidal composition as claimed in Claim 11, wherein the active material is cuprous O-isopropyl phosphonate.
25. A fungicidal composition as claimed in Claim 11, wherein the active material is cupric O-isopropyl phosphonate.
26. A fungicidal composition as claimed in any of Claims 1 to 25 which additionally contains a known fungicide.
27. A fungicidal composition as claimed in Claim 1, substantially as herein described with reference to any of the specific Examples.
28. A process for controlling fungus disease in plants, comprising applying a composition of the kind claimed in any of Claims 1 to 27 to the plant or to the environment of the plant.
- 30 29. A process as claimed in Claim 28 substantially as herein described with reference to any of the specific Examples.

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