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"FUNGICIDAL COMPOSITION BASED ON ALUMINIUM TRIS-(ETHYL PHOSPHONATE)"

The present invention relates to new fungicidal
5 compositions based on a phosphorous acid ester, and to a
method of combating fungal diseases of plants with the aid
of these compositions.

French Patent 2,254,276 describes compositions for
combating fungal diseases of plants, which contain, as the
10 active ingredient, at least one salt of an alkyl-phosphorous
acid. These compositions are effective against many
phytophagous fungi, such as Phycomycetes, in particular
Plasmopara viticola and various Phytophthora. In practice,
aluminium ethyl phosphite [which may also be named as
15 "aluminium tris-(ethyl phosphonate)" and which is hereinafter
identified as "phosethyl Al"] is used commercially, in the
form of a wettable powder, for treatment by spraying the
leaves. Although this formulation is quite effective under
these conditions, in particular for protecting vines, its
20 effectiveness takes longer to appear when it is applied
curatively to tropical crops attacked, often heavily, by
fungi of the Phytophthora type, such as Phytophthora cinnamomi
which cause avocado rot or rot of citrus fruits.

25 In fact, the amounts absorbed by a foliage of low
absorbency are relatively small, and are insufficient if
trees which have already been attacked are treated
curatively. This necessitates more applications, rendering
the treatment prohibitive, slow in all respects and even
30 inadequate in view of the severity of the attack by the fungi.

It has now been found that these diseases can be effectively combated by application, in particular by injection into the trunks of trees, of a stabilised aqueous solution of phosethyl Al. However, this poses a problem
5 inasmuch as this active ingredient undergoes hydrolysis in an aqueous medium which substantially and progressively decreases its concentration, making it impossible to obtain concentrated aqueous compositions which are stable over a period of time.

10 The present invention provides a process for stabilising aqueous solutions of phosethyl Al, which comprises adding a water-soluble salt of a weak acid and a strong base, as the stabiliser, to the aqueous solution of phosethyl Al. The invention also relates to aqueous solutions of
15 phosethyl Al stabilised by this process. The term "weak acid" is to be understood as meaning a mineral acid, such as acid salts of phosphorous acid or phosphonic acid or, preferably, an organic acid, such as, e.g., an aliphatic acid, for example acetic acid, propionic acid, butyric
20 acid, fumaric acid, oxalic acid, lactic acid or citric acid, or an aminoacid, for example ethylenediaminetetracetic acid.

Strong bases which may be used are organic bases, such as a tertiary amine, or, preferably, mineral bases,
25 such as alkali metal hydroxides and alkaline earth metal hydroxides, preferably with a good solubility in water, such as sodium hydroxide, potassium hydroxide or lime.

The amount of stabiliser depends on the nature thereof and the concentration of phosethyl Al in the aqueous

composition. In fact, if the stabiliser is present either in too small an amount or, on the other hand, in too large an amount, the solution is not clear which signifies that solubilisation of the active ingredient is insufficient, with the result that the effectiveness is correspondingly limited. Surprisingly, it has moreover been found that the most suitable amount is not that corresponding to the stoichiometric amount which, if the stabilising agent is calcium acetate, is 2 phosethyl Al:3 calcium acetate. For example, in the case of calcium acetate, about half the stoichiometric amount gives a stable clear solution, whilst twice this amount gives rise to a precipitate. The compositions according to the invention are preferably prepared by adding a water-soluble salt of the weak acid and the strong base, e.g. calcium acetate, to an aqueous solution of the phosethyl Al.

The aqueous composition according to the invention may also contain other water-soluble adjuvants, such as surface-active agents, although this is not necessary for injectable solutions. It may also contain certain oligo-elements which promote growth of the trees or are advantageous in combating deficiencies, such as salts of zinc, manganese, iron or boron in suitable amounts.

The phosethyl Al is present in the compositions according to the invention in a concentration of in general between 1 and 120 g/litre and preferably between 10 and 110 g/litre.

This solution can be applied to plants to combat attacks by phytophagous fungi by any suitable treatment, such as spraying of the leaves or soaking of the roots. Excellent results have been obtained by injection into the

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trunk of diseased trees, such as, e.g., avocado trees, but the process can be applied to other trees, such as citrus fruit trees, or hevea or cocoa trees. The treatment is carried out by first making holes distributed around the trunk of the tree.

In a second stage, a defined amount of the aqueous phosethyl Al solution employed, which may vary from 0.1 to 5 g/m² of soil covered by the foliage, is injected into the holes with any appropriate device, with or without using pressure.

The liquid is absorbed slowly and is preferably kept under pressure in the injection apparatus. When the injection has ended, it may be desirable to block the hole or holes with the aid of a material which is non-aggressive towards the plant tissue, such as, e.g., a wax, which may contain adjuvants, such as disinfectants, in order to reduce the risk of introducing secondary diseases. The number of treatments is very small, especially with respect to the number of interventions necessary when the leaves are sprayed. For example, on a severely attacked tree, effective curative treatment is obtained in the first year with two injections, and in the following years treatment once per year is sufficient to keep the tree healthy or on the way to recovery. The effectiveness of the treatment is remarkable, heavily attacked trees being cured within 2 years, which is surprising since other systemic fungicides which are usually active on these fungi are ineffective when injected under the same conditions.

The examples which follow illustrate the preparation

of compositions according to the invention.

Example 1:

The three following compositions, where quantities are by weight, are prepared by dissolving successively
5 phosethyl Al and, where appropriate, calcium acetate in water:

	<u>Control Composition</u>	<u>Composition of the Invention</u>	
		1	2
Technical grade 98% pure			
10 phosethyl Al	102	102 ...	102
Calcium acetate	-	33 ...	67
Water qsp 1 litre	898	865 ...	831

The amounts of acetate added to Compositions 1 and 2 correspond respectively to half the stoichiometric amount,
15 for composition 1, and to all of this stoichiometric amount, for composition 2.

The three solutions are subjected to a stability test at 50°C for 1 month, after which the relative degradation of phosethyl Al and the appearance of the
20 solution are evaluated. The results are shown in the following table:

Evaluation criterion after 1 month at 50°C	Control Composition	Composition of the invention	
		1	2
25 Relative degradation of phosethyl Al	100%	12%	12%
Appearance of the solu- tion (initially clear)	precipitate	clear	precip- itate

This table clearly shows that after 1 month at 50°C:

- in the control solution, the phosethyl Al is completely degraded and a precipitate forms in the solution. This solution is thus neither stable nor clear;
- in solutions 1 and 2 according to the invention, the degradation of phosethyl Al is limited in an acceptable manner; moreover, whilst a slight precipitate has formed in solution 2, solution 1 is clear. Thus only solution 1 is completely satisfactory.

Example 2:

Two compositions are prepared by diluting composition 1, obtained in Example 1, once and, respectively, twice. Compositions containing, respectively, 51 and 20.5 grams of 98% pure phosethyl Al and 16.5 and 8.25 grams of calcium acetate are thus obtained.



CLAIMS

1. A fungicidal composition which comprises an aqueous solution of phosethyl Al containing, as the stabilising agent, a salt of a weak acid and a strong base.
- 5 2. A composition according to claim 1 in the form of a clear aqueous solution.
3. A composition according to claim 1 or 2 wherein the weak acid is an organic acid.
4. A composition according to 1 or 2 wherein the
10 weak acid is an aliphatic acid or an aminoacid.
5. A composition according to claim 1 or 2 wherein the weak acid is acetic acid, propionic acid, butyric acid, fumaric acid, oxalic acid, lactic acid, citric acid or ethylenediaminetetracetic acid.
- 15 6. A composition according to any one of claims 1 to 5 wherein the strong base is calcium hydroxide.
7. A composition according to any one of claims 1 to 5 wherein the strong base is sodium hydroxide or potassium hydroxide.
- 20 8. A composition according to any one of claims 1 to 5 wherein the stabiliser is calcium acetate.



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9. A composition according to claim 1 in the form of a clear aqueous solution which comprises an aqueous solution of phosethyl Al containing, as stabiliser, half the stoichiometric amount of calcium acetate, the stoichiometric amount being defined as 4 phosethyl Al : 3 calcium acetate.

10. A composition according to any one of claims 1 to 9, which contains from 1 to 120 g/litre of phosethyl Al.

11. A composition according to claim 1 substantially as hereinbefore described with especial reference to Example 1 or 2.

12. A process for obtaining stable aqueous solutions containing phosethyl Al according to any one of claims 1 to 11, which comprises adding a water-soluble salt of a weak acid and strong base to these solutions.

13. A process according to claim 12 substantially as hereinbefore described with especial reference to Example 1.

14. A method for combating attacks by phytophagous fungi on crop plants which comprises applying to the plants an effective amount of a composition according to any one of claims 1 to 11.

15. A method for combating attacks by phytophagous fungi on crop trees which comprises injecting an effective amount of a composition according to any one of claims 1 to



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11 into the trunk of the tree.

16. A method according to claim 15 wherein the crop tree is avocado.

17. A method according to claim 15 substantially 5 as hereinbefore described.
