

L178.850

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

4,4'-Dibromo-Benzilic Acid and Esters and Acaricidal and Insecticidal Composition containing them

We, AGRIPAT S.A., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, 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:—

The present invention relates to 4,4' - dibromo - benzilic acid isopropyl ester, its production and acaricidal and insecticidal compositions which contain this ester as active substance, as well as processes for the production of these compositions and processes for combatting spiders and insects by using the new active substance.

Esters of 4,4' - dichlorobenzilic acid and their use for the combatting of spiders and insects are known from Swiss patent No. 294,599. These esters are, however, relatively toxic to warm blooded animals and are phytotoxic to various cultivated plants such as fruit cultivations. In addition, after the use of these known benzilic acid esters for a longer time, various spiders showed noticeable signs of resistance.

Surprisingly, it has now been found that 4,4' - dibromobenzilic acid isopropyl ester is excellently suitable for the control of spiders and insects and also their stages of development. In comparison with known benzilic acid esters, the new active substance has a much lower toxicity to warm-blooded animals. The DL_{50} for rats is over 5,000 mg of active substances per kg body weight, while the acute toxicity of the known 4,4' - dichloro - benzilic acid ethyl ester is about 2,200 mg/kg.

The known acaricidally active substances

4,4' - dichloro - benzilic acid ethyl ester and 4,4' - dichlorobenzilic acid isopropyl ester, cause phytotoxic effects in various types of fruit trees, for instance, peach trees, plum trees and apple trees even in the usually applied concentrations, while no phytotoxic effects are registered with a 0.05% suspension of the new compound on plants and fruit trees even after they have been treated four times.

The new 4,4' - dibromobenzilic acid isopropyl ester is suitable for the combatting of normally sensitive and resistant mites on plants, trees and animals. Its action is particularly marked against Tetranychidae, not only against the mobile stages thereof (larvae, protonymphs, deutonymphs, adults), but also against the dormant stages (nymphochrysalis, deutochrysalis, teileiochrysalis) and especially against the eggs.

In order to test the acaricidal properties of the new compound, two series of tests were carried out with bean leaves infected with red spider mites (*Tetranychus urticae*) and all stages of their development. The bean leaves were treated with an aqueous emulsion containing 0.005% of 4,4' - dibromo - benzilic acid isopropyl ester (prepared from 25% emulsion concentrate). After 6 days, the mortality of all stages and the oviposition were determined and expressed in percent.

Red spider mites which were normally sensitive and resistant to known benzilic acid esters and phosphoric acid esters were taken as test animals. The new compounds, i.e. 4,4' - dibromo - benzilic acid isopropyl ester was compared with the known 4,4' - dichlorobenzilic acid isopropyl ester. The test results are given in the following table.

TABLE 1

Stages of the test animals	Stock of spider mites	% of animals killed	
		4,4'-dichloro-benzilic acid isopropyl ester	4,4'-dibromo-benzilic acid isopropyl ester
Adults Dormant stages Eggs	Normal sensitive	100 ; 100 60 ; 20 50 ; 30	100 ; 100 100 ; 100 100 ; 100
Adults Dormant stages Eggs	Resistant to 4,4'-dichlorobenzilic acid ethyl ester	99 ; 98 50 ; 60 60 ; 60	100 ; 100 100 ; 100 95 ; 95
Adults Dormant stages Eggs	Resistant to 0,0-diethyl-S-(2,5-dichlorophenyl-thiomethyl)-dithio-phosphate	100 ; 99 30 ; 50 30 ; 50	100 ; 100 100 ; 98 98 ; 95
Adults Dormant stages Eggs	Resistant to 0,0-diethyl-0-(2-isopropyl-4-methyl-6-pyrimidyl)-thio-phosphate	95 ; 100 60 ; 70 60 ; 60	100 ; 100 100 ; 100 100 ; 99

These results clearly show that even in this low concentration, the new compound effects an almost 100% killing of the mites and all stages of their development, whereas the known compounds show the required results only against living stages but lacks sufficient effectiveness against dormant stages and eggs of the mites. Thus, the known compound is insufficient because the survival of eggs and dormant stages will readily cause a new infestation because the surviving animals will readily proliferate.

It has also been determined that the 4,4'-dibromo - benzilic acid isopropyl ester according to the invention has a good action against eating insects such as, e.g. insects of the families Curculionidae, Bruchididae, Dermestidae, Tenebrionidae and Chrysomelidae, e.g.

granary weevils (*Sitophilus granaria*), bean beetles (*Bruchidius obtectus*), larder beetles (*Dermestes vulpinus*), yellow mealworms (*Tenebrio molitor*) and especially against potato beetles (*Leptinotarsa decemlineata*), and their larval stages.

Potato plants infested with all stages of larvae of the potato beetle were treated with a 0.04% aqueous solution of 4,4' - dibromobenzilic acid isopropyl ester and a 0.04% aqueous solution of 4,4' - dichloro - benzilic acid isopropyl ester.

The living larvae on the potato plants were counted one day and eight days after the treatment with the above-mentioned solutions. The test results are given in the following table.

TABLE II

Compound tested	Number of potato plants treated	Number of plants infested	
		after 1 day	after 8 days
4,4'-dibromobenzilic acid isopropyl ester	28	1 (0 to 10 larvae per plant)	0
4,4'-dichlorobenzilic acid isopropyl ester	28	10 (0 to 10 larvae per plant)	10 (6 plants with 0 to 10 larvae per plant)
control (untreated)	14	14 (10 to 50 larvae per plant)	14 (4 plants with 0 to 10; 3 plants with 10 to 50 and 7 plants with more than 50 larvae per plant)

These test results clearly show the excellent insecticidal activity of the new compound.

4,4'-dibromobenzilic acid isopropyl ester is obtained according to the invention by esterifying 4,4'-dibromobenzilic acid with isopropanol or an isopropyl halide in the presence of an acid or base and, optionally, in the presence of a solvent which is inert to the reaction partners. The new ester is crystalline and melts at 76—79°C. The 4,4'-dibromobenzilic acid is prepared by reacting 4,4'-dibromobenzil with e.g. an alcoholic sodium or potassium hydroxide solution.

4,4'-dibromobenzilic acid isopropyl ester is applied in the form of solid or liquid compositions such as dusts, sprinkling agents, granulates, aqueous dispersions which are obtained from wettable powders, pastes, emulsion concentrates, also as solution or aerosol. Wettable powders and emulsion concentrates are preferred.

The agents according to the invention are produced in the known way by intimately mixing and milling the active substance with suitable carriers. Dispersing agents or solvents which are inert to the active substance may be added. The concentration of active substance in these compositions is, e.g. 0.01 to 80%, preferably 10% to 80%. The compositions according to the invention can be used together with acaricidal, insecticidal, ovicidal, fungicidal, bactericidal compounds and/or with synergists to inactive additives. These concentrates can be diluted to give the desired concentrations for application, preferably from 0.01% to 1%.

The following Examples 1 and 2 describe the production of the new active substance; thereafter forms for application are described in which the active substance can be used in plant protection. Where not otherwise expressly stated, parts are given as parts by

weight and the temperatures are in degrees Centigrade.

EXAMPLE 1

15 Parts of 4,4'-dibromobenzilic acid (prepared by reacting 4,4'-dibromobenzil with an alcoholic sodium hydroxide solution) and 2,2 parts of pulverised potassium hydroxide are dissolved while heating in 150 parts by volume of dimethyl formamide. 6.6 Parts of isopropyl iodide are then added dropwise to this solution while stirring. The reaction mixture is then heated for 5 hours at 50—60° while continuously stirring. The suspension is then poured into ice water and the precipitate formed is filtered off under suction, washed neutral with water and dried. Recrystallised from petroleum ether, the 4,4'-dibromo-benzilic acid isopropyl ester melts at 76—79°.

If, instead of 6.6 parts of isopropyl iodide, 3,4 parts of isopropyl chloride are used, then 4,4'-dibromobenzilic acid isopropyl ester is also obtained. It melts at 76—79°.

EXAMPLE 2

1.08 Parts of concentrated sulphuric acid and 47 parts of isopropanol are added to a solution of 123.5 parts of 4,4'-dibromobenzilic acid in 300 parts by volume of abs. benzene and the solution is refluxed for 25 hours while separating off water. Finally, water is added to the reaction mixture, the benzene solution is washed neutral and dried over sodium sulphate. After distilling off the solvent, the crystalline residue is recrystallised from petroleum ether. The 4,4'-dibromobenzilic acid isopropyl ester melts at 76—79°.

Dust

To produce a 10% dust, 10 parts of 4,4'-dibromobenzilic acid isopropyl ester,

5 parts of highly dispersed silicic acid and 85 parts of talcum are intimately mixed. Such a dust can be used, e.g. for combatting spider mites on vegetables and ornamentals as well as on woody ornamentals and berry-bearing shrubs.

Wettable Powder

To produce a) a 50% and b) a 10% wettable powder, the following components are used:

a)
50 parts of 4,4' - dibromobenzilic acid isopropyl ester
5 parts of oleoyl methyl tauride Na salt
2.5 parts of dinaphthalene methane disulphonic acid disodium salt
25 parts of calcareous earth-clay silicates
17.5 parts of kaolin

b)
10 parts of 4,4' - dibromobenzilic acid isopropyl ester
3 parts of a mixture of sodium salts of saturated fatty alcohol sulphonates (fatty alcohols = C_8-C_{18})
5 parts of dinaphthalene methane disulphonic acid disodium salt
82 parts of kaolin

The amounts of active substance mentioned are intimately mixed in suitable mixers with the additives and milled in corresponding mills and rollers. Wettable powders are obtained which can be diluted with water to form suspensions of any concentration desired. Such suspensions are mainly used for combatting spider mites in stone and pome fruit trees, ornamentals of all types, vegetables, woody ornamentals and berry-bearing shrubs.

Emulsion concentrates

To produce a) a 50% and b) a 25% emulsion concentrate, the following components are mixed together:

a)
50 parts of 4,4' - dibromobenzilic acid isopropyl ester
17.5 parts of 2 - methoxyethanol
22.5 parts of xylene
8 parts of nonylphenol polyglycol ether condensate
2 parts of dodecylbenzene sulphonate calcium salt

b)
25 parts of 4,4' - dibromobenzilic acid isopropyl ester
10 parts of diacetyl alcohol
2 parts of alkylaryl polyglycol ether
3 parts of an emulsion combination (nonylphenol polyoxyethylene - dodecylbenzene sulphonic acid calcium salt)
60 parts of xylene.

These concentrates can be distilled with water to form emulsions of any concentration desired. Such emulsions are used, e.g. to com-

bat *Tetranychus urticae*, *Metatetranychus ulmi* and *Bryobia pretiosa* (common spider mite, fruit tree spider mite and red gooseberry spider mite) on plum trees (Fellenberg, Basler Zwetschgen, Reineclauden, Bühler Zwetschgen and Mirabellen).

Paste

The following substances are used to produce a 45% paste:

45 parts of 4,4' - dibromobenzilic acid isopropyl ester
5 parts of sodium aluminium silicate
14 parts of cetyl polyglycol ether (condensate from saturated C_8-C_{18} fatty alcohols with 8 mols of ethylene oxide)
1 part of oleyl polyglycol ether (oleyl alcohol + 5 mols of ethylene oxide condensate)

2 parts of spindle oil
10 parts of polyethylene glycol ether ("Carbowax")
23 parts of water.

The active substance is intimately mixed and milled with the additives in suitable apparatus. A paste is obtained from which, by dilution with water, suspensions of any concentration desired can be produced. Such suspensions are used, in particular, for combatting spider mites on useful plants and ornamentals and also on fruit trees.

WHAT WE CLAIM IS:—

1. 4,4' - dibromobenzilic acid isopropyl ester.

2. 4,4' - dibromobenzilic acid.

3. Acaricidal and insecticidal agent, which comprises as active substance, 4,4' - dibromobenzilic acid isopropyl ester in admixture with carriers and/or distributing agents and/or other active ingredients.

4. Process for the production of 4,4' - dibromobenzilic acid isopropyl ester, which comprises esterifying 4,4' - dibromobenzilic acid with isopropanol or an isopropyl halide.

5. Process for the production of acaricidal and insecticidal agents, which comprises milling 4,4' - dibromobenzilic acid isopropyl ester with and dispersing it in carriers and/or distributing agents.

6. Process for combatting spiders and insects which comprises contacting said spiders and/or insects and/or their habitats with 4,4' - dibromobenzilic acid isopropyl ester or with agents containing it.

7. An acaricidal and insecticidal agent as claimed in claim 3 substantially as hereinbefore described in any one of the Examples.

8. A process as claimed in claim 6 substantially as hereinbefore described in any one of the Examples.

9. A process as claimed in claim 6 substantially as hereinbefore described with reference to the Examples and Tables I and II.

- 5 parts of highly dispersed silicic acid and 85 parts of talcum are intimately mixed. Such a dust can be used, e.g. for combatting spider mites on vegetables and ornamentals as well as on woody ornamentals and berry-bearing shrubs.

Wettable Powder

- To produce a) a 50% and b) a 10% wettable powder, the following components are used:

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 - 2.5 parts of dinaphthalene methane disulphonic acid disodium salt
 - 25 parts of calcareous earth-clay silicates
 - 17.5 parts of kaolin
- b)
- 10 parts of 4,4' - dibromobenzilic acid isopropyl ester
 - 3 parts of a mixture of sodium salts of saturated fatty alcohol sulphonates (fatty alcohols = C_8-C_{18})
 - 5 parts of dinaphthalene methane disulphonic acid disodium salt
 - 82 parts of kaolin

- The amounts of active substance mentioned are intimately mixed in suitable mixers with the additives and milled in corresponding mills and rollers. Wettable powders are obtained which can be diluted with water to form suspensions of any concentration desired. Such suspensions are mainly used for combatting spider mites in stone and pome fruit trees, ornamentals of all types, vegetables, woody ornamentals and berry-bearing shrubs.

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- b)
- 25 parts of 4,4' - dibromobenzilic acid isopropyl ester
 - 10 parts of diacetonyl alcohol
 - 2 parts of alkylaryl polyglycol ether
 - 3 parts of an emulsion combination (nonylphenol polyoxyethylene - dodecylbenzene sulphonic acid calcium salt)
 - 60 parts of xylene.

- These concentrates can be distilled with water to form emulsions of any concentration desired. Such emulsions are used, e.g. to com-

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- 10 parts of polyethylene glycol ether ("Carbowax")
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WHAT WE CLAIM IS:—

1. 4,4' - dibromobenzilic acid isopropyl ester.
2. 4,4' - dibromobenzilic acid.
3. Acaricidal and insecticidal agent, which comprises as active substance, 4,4' - dibromobenzilic acid isopropyl ester in admixture with carriers and/or distributing agents and/or other active ingredients.
4. Process for the production of 4,4' - dibromobenzilic acid isopropyl ester, which comprises esterifying 4,4' - dibromobenzilic acid with isopropanol or an isopropyl halide.
5. Process for the production of acaricidal and insecticidal agents, which comprises milling 4,4' - dibromobenzilic acid isopropyl ester with and dispersing it in carriers and/or distributing agents.
6. Process for combatting spiders and insects which comprises contacting said spiders and/or insects and/or their habitats with 4,4' - dibromobenzilic acid isopropyl ester or with agents containing it.
7. An acaricidal and insecticidal agent as claimed in claim 3 substantially as hereinbefore described in any one of the Examples.
8. A process as claimed in claim 6 substantially as hereinbefore described in any one of the Examples.
9. A process as claimed in claim 6 substantially as hereinbefore described with reference to the Examples and Tables I and II.



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