

1342 630

PATENT SPECIFICATION

(11) 1342 630

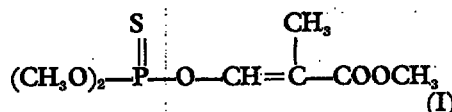
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(54) PHOSPHOROTHIONATE HAVING INSECTICIDAL AND ACARICIDAL PROPERTIES

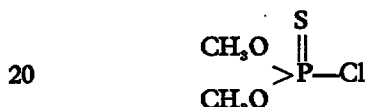
(71) We, CIBA-GEIGY AG, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to O,O-dimethyl - 2 - carbomethoxy - 1 - propen - 1 - yl - phosphorothionate having the formula 1

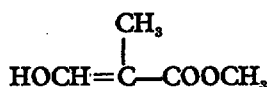


its manufacture and its use in the control of insects and members of the order Acarina and their development stages.

The compound according to the invention may be manufactured in a known manner by reacting O,O-dimethylthionophosphoric acid chloride having the formula



with α hydroxymethylenepropionic acid methyl ester having the formula



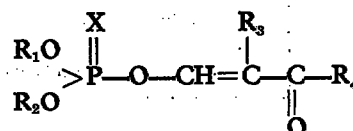
or preferably an alkali metal salt thereof, e.g. the sodium salt.

The reaction is generally carried out in an inert, preferably polar solvent such as dioxane, acetonitrile, dimethylsulfoxide, dimethylformamide, or for example benzene, toluene, xylene, chlorobenzene and others, at temperatures of 15 to 80° C, especially 30 to 70° C.

The compound of the formula I may be used in combating insects and members of the order Acarina and their development stages. It is particularly suitable for combating species of said insects and members of the order Acarina and their development stages which attack stored products and grains as it fulfills all the necessary requirements therefore namely:

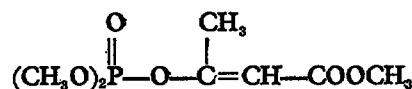
- 1) low minimum lethal concentration for insects etc.
- 2) low toxicity towards humans and domestic animals
- 3) a uniform action over many months
- 4) no residue problems
- 5) a faint characteristic smell.

Our British Patent No. 1,182,129 describes and claims compounds of the general formula:



in which R₁ and R₂ are identical or different lower alkyl groups, X is an oxygen or a sulphur atom, R₃ represents a hydrogen atom, a lower alkyl group or a halogen atom and R₄ represents a lower alkoxy group, a lower alkyl group or an unsubstituted or substituted aryl group.

It has been found that compared with the known analogous compounds disclosed in British Patent 1,182,129 and the commercial products PHOSDRIN (Registered Trade Mark) of the formula



[warmblooded toxicity LD₅₀ 3—7 mg/kg body

weight orally (rats)] and DDVP (dimethyldichlorovinylphosphate) [warmblooded toxicity LD₅₀ 50 mg/kg body weight orally (rats)], the compound of the formula I exhibits not only a surprisingly low toxicity of LD₅₀ 500 mg/kg orally (rats), but also has the advantage of stronger activity, long effective life and easy diffusion in stored grains etc. as can

be seen in the biological tests given herein. Furthermore, it presents few residue problems and has a faint characteristic smell.

By virtue of these properties and in particular its low toxicity the compound of the formula I is suitable for combating the following storage and crop pests.

Latin Name	Common Name
<i>Oryzaephilus surinamensis</i>	Saw-toothed grain beetle
<i>Trogoderma granarium</i>	Knapra beetle
<i>Lasioderma serricorne</i>	cigarette beetle
<i>Chryptolestes ferrugineus</i>	rust-red grain beetle
<i>Stegobium paniceum</i>	biscuit beetle
<i>Necrobia rufipes</i>	Copra beetle
<i>Anthrenus vorax</i>	carpet beetle
<i>Sitophilus granarium</i>	grain weevil
<i>Sitophilus oryzae</i>	lesser rice weevil
<i>Sitophilus zeamais</i>	greater rice weevil
<i>Rhizopertha dominica</i>	lesser grain borer
<i>Acanthoscelides obtectus</i>	dried bean beetle
<i>Sitotroga cerealella</i>	Angoumois grain moth
<i>Nemapogon granellus</i>	corn moth
<i>Tyrophagus putrescentiae</i>	copra mite

Latin Name	Common Name
<i>Acarus siro</i>	flour mite
<i>Ephestia kuehniella</i>	mediterranean flour moth
<i>Araecerus fasciculatus</i>	coffee bean weevil
<i>Carpophilus hemipterus</i>	dried fruit beetle
<i>Tenebrio molitor</i>	Yellow mealworm beetle
<i>Tribolium castaneum</i>	rust-red flour beetle
<i>Tribolium destructor</i>	dark flour beetle
<i>Tribolium confusum</i>	confused flour beetle
as well as cockroaches such as	
<i>Blattella germanica</i>	German cockroach
<i>Periplaneta americana</i>	American cockroach
<i>Blatta orientalis</i>	Oriental cockroach

The active substance of formula I can be used as pure concentrate or in admixture or conjunction with suitable carriers and/or adjuvants and can be applied to the pests or the locus thereof or can be applied as a protective measure before storage.

Suitable carriers and adjuvants can be solid or liquid and correspond to the substances conventionally used in formulation techniques, for example natural or regenerated mineral substances, solvents, dispersants, wetting agents, adhesives, thickeners, binders or fertilisers.

The active substance of formula I can be used in pure form, for example by treating warmed containers with the agent and allowing the contents to evaporate.

The active substance can also be formulated in customary solid or liquid fashion and can be used as an emulsion concentrate, spraying powder, dusting powder, granulate or spray. Of primary use are gas phase, fumigation or sprayed applications. In this way crops such as wheat, rye, barley, oats, millet, rice, maize, and other dried fruits can be treated during filling into silo storage, for example on a conveyor belt, with a liquid formulation of the material of formula I.

Sprayable solutions suitable for direct application contain e.g. mineral oil fractions of high to medium boiling range, particularly over 100° C, such as diesel oil or kerosene and furthermore coal tar oil or vegetable or animal oils, together with hydrocarbons such as alkylated naphthalene, tetrahydronaphthalene, xylene mixtures, cyclohexanols, and optionally

in addition ketones, chlorinated hydrocarbons such as tetrachloroethane, trichloroethylene, or tri- and tetrachlorobenzenes.

For use in aqueous application forms, emulsion concentrates, pastes or wettable spraying powders are used with the addition of water. As emulsifiers or dispersants there can be used non-ionogenic products, e.g. condensation products of aliphatic alcohols, amines or carboxylic acids with a long chain hydrocarbon residue of from 10 to 30 carbon atoms with ethylene oxide, for example the condensation product of octadecyl alcohol and 25 to 30 mols ethyleneoxide, or that of soya fatty acid and 30 mols ethylene oxide or that of technical oleylamine and 15 mols ethylene oxide or that of dodecylmercaptan and 12 mols ethylene oxide. However condensation products of ethylene oxide with hydroaromatic-polycyclic carboxylic acids and amines can also be used. Amongst anionic emulsifying agents which may be used there should be mentioned: the sodium salt of dodecylalcoholsulphonate esters, the sodium salt of dodecylbenzenesulfonic acid, the potassium or triethanolamine salt of oleic acid or of abietic acid or of mixtures of these acids, or the sodium salt of a petroleum sulphonic acid. As cationic dispersing agents, there can be used quaternary ammonium and phosphonium compounds, e.g. cetylpyridinium-chloride or dioxyethylbenzylododecylammonium chloride. If the active substance of the invention is to be used in the form of a dusting or scattering preparation, then it can contain talcum, kaolin, bentonite, sand, calcium car-

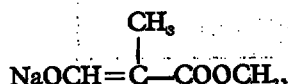
- bonate, calcium phosphate or even coal as solid carrier materials. Evaporating agents can also be added to the stored goods such as, for example, porous clay bars impregnated with the active agent. The various preparations can contain in customary fashion the addition of materials which improve the distribution, the adhesive strength, or the penetration depth; among such materials should be mentioned fatty acids, resins, glues, casein, or e.g. alginates. The use of preparations in granulated form is also very useful. The compound of the invention can be present as sole active material in the pest control agents, or it may be in combination with other insecticides or acaricides.

The following Examples illustrate the invention. All parts and percentages given are by weight.

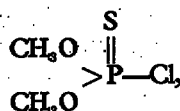
20 Example 1.

Preparation

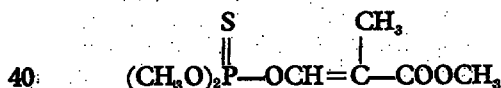
27.6 parts of the sodium salt of α -hydroxymethylenepropionic acid methyl-ester,



- 25 were warmed in 200 parts by volume of acetonitrile to 40–50° C. At this temperature, 33 parts of O,O-dimethyl-thionophosphoric acid chloride,



- 30 were added dropwise and the mixture then maintained for 4 hours with stirring at 40–50° C. After cooling, the salts were filtered off with suction and the solvent removed in vacuo at 50° C bath temperature. The residue was taken up in methylene chloride and rinsed with N caustic soda. After the evaporation of the solvent in vacuo O,O-dimethyl-2-carbomethoxy - 1 - propen - 1 - yl - phosphorothionate of the formula



was obtained in the form of an oil.

The compound boiled at 80–90° C (0.01 mm Hg).

Example 2.

45 Compositions

A. *Dusting agent*: Equal parts of the active agent according to the invention and precipitated silica were finely ground. By mixing with kaolin or talcum, it was possible to

manufacture dusting agents with the preferred 1–6% content of active substance.

B. *Powder for spraying*: For the manufacture of a water soluble spraying powder, the following components were mixed and finely ground:

- 50 parts active agent of formula I
- 20 parts highly absorbent silica
- 25 parts Bolus alba (Kaolin)
- 1.5 parts sodium 1-benzyl-2-stearylbenzimidazol-6,3'-disulphonate
- 3.5 parts of a reaction product of p-tert-octylphenol and ethyleneoxide.

C. *Emulsion concentrates*: a) 40 parts of the active substance of formula I were mixed with 40 parts of a mixture of an anionic surface active compound, preferably the calcium or magnesium salt of monolaurylbenzenemonosulphonic acid, and a nonionic surface active compound, preferably a polyethyleneglycol-ether of monosorbitollaureate, and the whole dissolved in a little xylene. The solution was then made up with xylene to 100 ml and a clear solution was thus obtained which could be used as a spraying agent concentrate and which gave a stable emulsion on being poured into water; b) it was also possible to formulate an emulsion concentrate according to the following instruction:

- 20 parts active agent
- 70 parts xylene

10 parts of a mixture of a reaction product of an alkylphenol with ethylene oxide and calcium dodecylbenzenesulphonate were mixed together. On dilution with water to the desired concentration, a sprayable emulsion resulted.

D. *Granulate*: 7.5 grams of the active agent of formula (1) were dissolved in 100 ml acetone and the so obtained acetonic solution added to 92 grams of coarsely granulated attapulgite.

The whole was well mixed and the solvent was removed in a rotary evaporator. A granulate was obtained with 7.5% active substance content.

Example 3.

Biological Tests

A) Gas Action against adult houseflies

Using a pipette 10 mg of active substance were placed on a watch glass which was then covered with a wire mesh and placed in a 2 liter glass cylinder. Immediately thereafter 30 houseflies were introduced into the container which was then sealed.

A comparative test between compound 1 and PHOSDRIN (Registered Trade Mark) carried out according to this method gave the following mortality periods in minutes for 10%, 50% and 100% kill of the test animals.

Active substance	Mortality time for a percentage kill of the houseflies			Acute oral toxicity LD ₅₀ (mg/kg) (rats)
	10%	50%	100%	
Phosdrin (Registered Trade Mark)	22'	25'	30'	3—7
Compound I	5'	8'	25'	500

B) Ingestion test with one day old houseflies (*Musca domestica*)

5 Dilution series were manufactured with water. As solvent for the test preparations and similarly as a nutrition agent for the flies, 30% sugar water was used which had been coloured with chlorantin light red (as an attractant).

The dilutions were tested with one day old houseflies. The 1, 2 and 4 hours controls enabled the speed of action to be determined. By means of the 24 hours control the limit concentration (action strength) could also be determined.

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Active Substance Concentration in 30% sugar water ppm	% flies killed by active agent							
	Phosdrin				Compound 1			
	after an exposure time of (hours)							
	1	2	4	24	1	2	4	24
100	100	100	100	100	100	100	100	100
50	30	70	80	100	60	90	100	100
25	20	40	60	100	40	70	100	100
12	0	0	20	90	40	70	100	100
6	0	0	10	80	30	40	100	100
3	0	0	0	20	10	20	50	90
1.5	0	0	0	0	0	0	0	10
0.8	0	0	0	0	0	0	0	0
0.4	0	0	0	0	0	0	0	0

C) Durability test between DDVP and Compound 1

Method:

20 Wheat was shaken up with 5% dusting agent and then half is mixed again repeatedly with an equal amount of untreated wheat to give half the concentration of active substance. In this way, a dilution series with concentrations of 50—25—12—6—3—1.5 ppm was obtained. In order to allow the duration differences between DDVP and Compound 1 to be demonstrated even better, the containers filled with the treated wheat (sized for 500

grams of wheat) were stored unsealed.

Since the test is repeated once per month, the desired information is obtained concerning the residual effect. In the test, the important pests in storage protection were chosen viz. the grain weevil (*Sitophilus granarius*)—lesser grain borer (*Rhizopertha dominica*) and the larvae of the Khapra beetle (*Trogoderma granarium*), which are very resistant to other insecticides. 20 test insects were tested per concentration and the results are expressed in the following table.

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20 test animals per concentration

Treated Wheat Stored For	Sitophilus granarius							Rhizopertha dominica							Trogoderma granarium (L.)						
	concentration of active substance in wheat (ppm)							concentration of active substance in wheat (ppm)							concentration of active substance in wheat (ppm)						
	50	25	12	6	3	1.5		50	25	12	6	3	1.5		50	25	12	6	3	1.5	
fresh	100	100	100	100	100	100		100	100	100	100	100	95		100	100	100	100	100	85	
1 month	100	100	100	25	5	0		100	65	15	10	5	0		100	75	5	0	0	0	
2 months	100	100	55	0	0	0		95	40	20	5	0	5		45	10	0	0	0	0	
3 months	95	50	0	0	0	0		80	15	0	0	0	0		0	0	0	0	0	0	
Compound 1																					
fresh	100	100	100	100	100	100		100	100	100	100	90	20		100	100	100	100	95	90	
1 month	100	100	100	100	100	90		100	100	85	60	5	0		100	100	95	85	10	0	
2 months	100	100	100	100	100	100		100	80	70	40	10	15		100	100	85	30	0	0	
3 months	100	100	100	100	95	70		100	75	35	15	15	0		100	100	55	10	0	0	
Control																					
fresh	0							0							0						
1 month	0							0							0						
2 months	0							5							0						
3 months	0							0							0						

Example 6.

D) Diffusion action in wheat

A "Plexiglass" ("Plexiglass" is a registered Trade Mark) box was divided by means of wire grids into ten vertical layers each 1 cm thick. Each compartment was filled with wheat grains. The first compartment contained

wheat grains which had been treated with 50 ppm active agent (5% dusting agent). The remaining compartments contained untreated wheat. All the compartments were then supplied with grain weevils. The mortality was noted after 7 days exposure time and the results are expressed in the following table.

Diffusion of active substance in gas phase between the wheat grains.
(Test Animal Sit. Granarius)

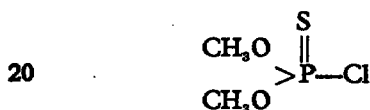
Distance in cm from the treated wheat layer	Mortality in % after 7 days exposure time with	
	DDVP	Compound I
1	100	100
2	100	100
3	80	100
4	0	100
5	0	90
6	0	15

WHAT WE CLAIM IS:—

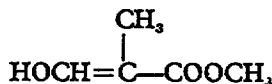
1. O,O-Dimethyl - 2 - carbomethoxy - 1-propen - 1 - yl phosphorothionate of the formula I



2. A process for the manufacture of the compound claimed in claim 1 which comprises reacting O,O-dimethylthionophosphoric acid chloride having the formula



with α hydroxymethylenepropionic acid methyl ester having the formula



or with an alkali metal salt thereof.

25 3. A process as claimed in claim 2 wherein said alkali metal salt is the sodium salt.

4. A process as claimed in claim 2 or 3 which is carried out at a temperature of between 15 and 80 °C.

5. An insecticidal or acaricidal composition which comprises as active ingredient a compound as claimed in claim 1 together with a suitable carrier and/or other adjuvant.

6. A method of combating insects and members of the order Acarina and their development stages which comprises applying thereto or to the locus thereof, as active substance, a compound as claimed in claim 1.

7. A method as claimed in claim 6 wherein said insects and members of the order Acarina and their development stages are such which attack stored crops, grains and similar products.

8. A method of protecting stored crops, grains and other similar products from attack by insects and members of the order Acarina and their development stages which comprises prior treatment with, as active substance, a compound as claimed in claim 1.

9. A composition as claimed in claim 5 substantially as hereinbefore described.

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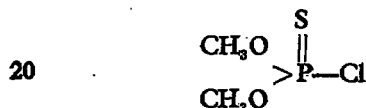
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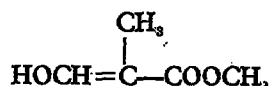
1. O,O-Dimethyl - 2 - carbomethoxy - 1-propen - 1 - yl phosphorothionate of the formula I



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