

PATENT SPECIFICATION

(11) 1242035

1242035

NO DRAWINGS

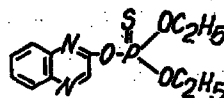
- (21) Application No. 974/70 (22) Filed 8 Jan. 1970
 (31) Convention Application No. P 19 03 228.1
 (32) Filed 23 Jan. 1969 in
 (33) Germany (DT)
 (45) Complete Specification published 11 Aug. 1971
 (51) International Classification A 01 n 9/36 // C 07 d 51/78
 (52) Index at acceptance
 A5E 1C4B3 1C4B4
 C2C 5A4 5E2
 (72) Inventors HEINRICH POHLMANN and KARL-JULIUS
 SCHMIDT



(54) INSECTICIDAL AND ACARICIDAL FORMULATIONS

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, 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:—

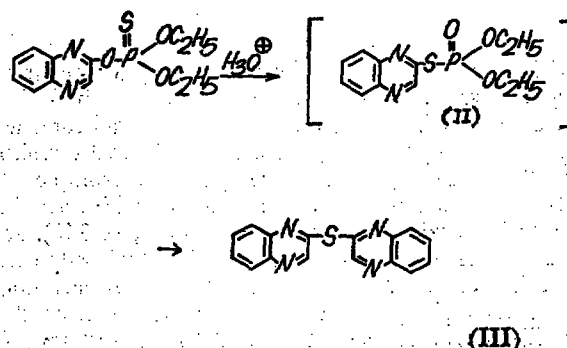
The present invention relates to certain new formulations of the known, insecticidally and acaricidally effective O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester (cf. British Patent Specification 1,081,249) of the formula



(I)

which exhibit an increased stability.

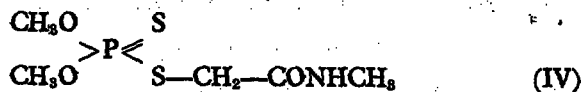
The above compound has proved to be unstable during storage, so that it loses a part of its insecticidal effectiveness, to an extent which depends on the temperature or the emulsifiers and solvents used. The mechanism of the degradation reaction is based on an initial isomerisation of the active compound (I) into presumably the thiol ester (II), which is converted into the monosulphide (III), with the splitting off of acidic phosphorus compounds, in accordance with the following presumed formula scheme:



(III)

The compound is sufficiently unstable to make its practical use as an insecticide or acaricide difficult or impossible. It is very desirable to provide some means of overcoming this difficulty.

It is known that similar re-arrangements can be avoided in the case of the N-monomethylamide of O,O-dimethyldithiophosphorylacetic acid (German Published Specification (D.A.S.) 1,175,939) of the formula

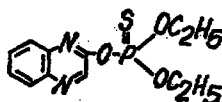


by the use of suitable solvents such as ethylene glycol monoethyl ether acetate, primary amyl acetate or cyclohexanone, possibly in admixture with hydrocarbons, such as xylene. The solvent proportion of the formulation is stated as about 75%.

Experiments which were carried out with O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester under the conditions stated did not, however, bring any improvement of the stability of this active compound beyond the known effect of stabilisation by dilution.

The present invention provides relatively stable formulations of this active compound.

The invention accordingly provides a formulation of the insecticidally and acaricidally effective O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester of the formula



(I)

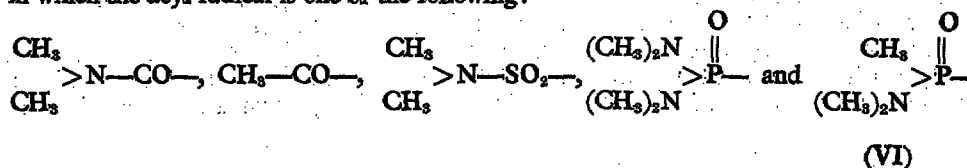
which contains

- (1) 20 to 80% by weight of the active compound
- (2) 15 to 80% by weight of inert, higher-boiling hydrocarbon, chlorinated hydrocarbon and/or ester as diluent, and
- (3) 0.1 to 10% by weight of tertiary amine and/or 0.01 to 10% by weight of stable dipolar aprotic solvent.

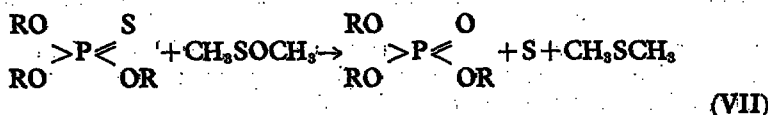
Preferred examples of dipolar aprotic solvents include dimethyl sulphoxide, N-methylpyrrolidone and compounds of the type



in which the acyl radical is one of the following:

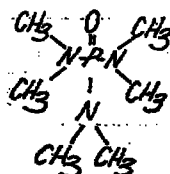


It is very surprising that the formulations according to the invention possess a high stability. It might have been expected that tertiary amines, in the conditions obtaining in practice, especially in the presence of air and moisture, would favour the decomposition of the active compound (I), since the ready hydrolysability of esters of this type in a weakly alkaline range is known (compare, for example, about the hydrolysis of O,O-diethyl-O-(4-nitrophenyl)-thionophosphoric acid ester in G. Schrader, "Die Entwicklung neuer insektizider Phosphorsäure-Ester", p. 240). It was further to be expected that the use of compounds such as dimethyl sulphoxide would also accelerate the degradation of the active compound. This disadvantageous effect of dimethyl sulphoxide on thionophosphoric acid esters is known from the literature (M. Mikolajczyk, Angew. Chem. 78, P. 393 (1966) and Chem. and Ind. 1966, P. 2059); it consists in an oxidation of the PS group according to the equation:



in which
R stands for lower alkyl.

It was therefore in no way to be foreseen that an addition of substantially smaller amounts of dimethyl sulphoxide would decisively improve the stability of the active compound (I) as the following experimental results show. It was, moreover, surprising that the phosphoric acid tris-dimethylamide of the formula



(VIII)

comparable to dimethyl formamide prevents the acidic decomposition of the active compound (I) for a time sufficient for practical purposes. Exploratory experiments with the solvent dimethyl formamide very commonly used in the art revealed no improvement of stability, irrespective of the proportions chosen. Dimethylformamide is not a dipolar aprotic solvent in the present context as it is not stable, especially any aqueous formulations where it is hydrolysed to formic acid and dimethyl amine.

The ability of the adjuvants to be used according to the invention, even in small amounts, to prevent for a substantial time the decomposition of O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester into bis-[quinoxalyl-(2)]-sulphide represents an enrichment of the art.

The diluents (ingredient (2)) are generally defined by the above designation. By "higher boiling" diluents are meant the usual diluents generally considered to have a relatively high boiling point, that is above 80°C. Most such diluents have a boiling point above that of water. As examples, there are mentioned chlorobenzene, toluene, xylene, phosphoric acid O,O,O-triethyl ester and amyl acetate. As indicated by the above examples, the esters may be of organic or inorganic acids.

Preferred stabilisers (ingredient (3)) include triethyl-amine, pyridine, N-methyl-piperidine, N,N-dimethyl-N-benzylamine, collidine, dimethyl sulphoxide, N-methyl-pyrrolidone, tetramethyl urea, dimethylacetamide, sulphuric acid bis-dimethylamide, phosphoric acid tris-dimethylamide and methane-phosphonic acid bis-dimethylamide.

Preferably, the active compounds are used in 20 to 30 or 50 to 80% by weight formulations. The content of diluent (ingredient (2)) is preferably 15 to 40 or 70 to 80% by weight. The tertiary amines to be used as stabilisers are preferably in amounts of 1 to 8 per cent by weight and the dipolar aprotic solvents 0.1 to 7% by weight.

The formulations may be used for combating insect and acarid pests in agriculture and elsewhere in known manner.

The invention therefore also provides a method of combating insect or acarid pests which comprises applying to the pests or a pest habitat a formulation according to the invention alone or diluted with a solid or liquid diluent or carrier.

The invention also provides crops protected from damage by insects or acarids by being grown in areas in which, immediately prior to and/or during the time of the growing, a formulation according to the invention is applied alone or in admixture with a solid or liquid diluent or carrier.

The formulation may be prepared by mixing ingredient (1) with ingredients (2) and (3).

The following Examples illustrate the present invention. Parts and percentages are by weight.

EXAMPLE 1

Qualitative stabilisation experiments.

Solutions of 80 parts of active compound and 17 parts of xylene were stored at 60°C. with, in each case, 3 parts of the stabilisers stated in Table 1, as well as (for comparison) without additive. At the intervals of time which can be seen from Table 1, samples were taken and investigated by thin-layer chromatography (system: silica gel HF, flow-medium: petroleum ether-acetone 9:1, detection: UV₂₅₄, PdCl₂). The experiment was broken off when the degradation product bis-quinoxalyl-(2)-sulphide occurred (Rf value 0.66 with reference to Rf value of the active compound as unity, mean from 5 chromatograms). In the following Table I, (—) means no bis-quinoxalyl-(2)-sulphide, (+) means traces, (++) means distinct amounts.

TABLE I
stabilising effect

Preparations	Days Storage at 60°C					
	13	28	44	61	79	107
Active compound (purest)						
80% in xylene (comparison)	—	+	++			
80% active compound + 17% xylene						
+ 3% dimethyl sulphoxide	—	—	—	—	—	—
+ 3% dimethyl benzylamine	—	—	—	—	—	++
+ 3% collidine	—	—	—	+	+	++
+ 3% N-methylpyrrolidone	—	—	—	—	+	++
+ 3% phosphoric acid tris-dimethylamide	—	—	—	—	—	—
+ 3% tetramethyl urea	—	—	—	—	+	++
+ 3% methanephosphonic acid bis-dimethylamide	—	—	—	+	+	+
+ 3% dimethylacetamide	—	—	—	+	++	
+ 3% sulphuric acid bis-dimethylamide	—	—	+	+	++	

EXAMPLE 2

Quantitative stabilisation experiments.

The solutions and formulations set forth in Table II were stored at 40°C.; their contents of active compound were determined at intervals of, in each case, four weeks, by thin-layer chromatography, IR spectroscopy and analytically. Chromatographically pure as well as technical-grade active compound was used.

TABLE II

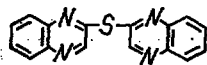
Degradation of various formulations of active compound

Preparations	Storage temperature: 40°C Content of active compound in % with reference to 100% initial active compound after weeks			
	0	4	8	12
20% formulation of the active compound (I) in xylene	99	87	76	46.5
cyclohexanone	96	30.5	15.5	
glycolmonoethyl ether acetate	98.5	85.5	75	46
amyl acetate	98	82	54.5	
dimethyl formamide	92	80	64	
dimethyl sulphoxide	69.5	15	7	
methylisobutyl ketone	95	76	38.5	
50% active compound (techn.) and 50% xylene	89.2	71.2		
80% active compound (techn.) and 20% xylene	92.6	68.7		
25% active compound (techn.) 30% emulsifier 3% dimethyl sulphoxide				
Remainder % xylene	95.2	88.8	—	84
25% active compound (techn.) 30% emulsifier 3% phosphoric acid tris-(dimethylamide)				
Remainder % xylene	96	90	—	89
25% active compound (techn.) 30% emulsifier 3% tetramethyl urea				
Remainder % xylene	97.6	93.2	87.2	78.8

15

Comparative Example

Preparation of bis-[quinoxalyl-(2)]-sulphide by decomposition of O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester.



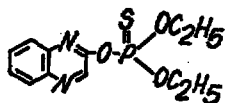
(III)

- 5 2580 g O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester were mixed 5
with 10 ml of 50% acetic acid and allowed to stand for three days in a drying cham-
ber at 60—70°C. Yellowish needles crystallised out. The decomposition mixture was
kept at -10°C. for several hours, the liquid components were filtered off with suction
and the solid residue was recrystallised from benzene-ligroin.
10 Yield: 792 g (62.5% of the theory) 10
bis-quinoxalyl-(2)-sulphide.
Melting point: 157—158°C.
Analysis:
Calculated for $C_{16}H_{10}N_4S$ (molecular weight 290.3)

15	C	H	N	S	15
	66.18%;	3.48%;	19.30%;	11.05%;	
	Found: 66.21%;	3.91%;	19.04%;	11.01%;	

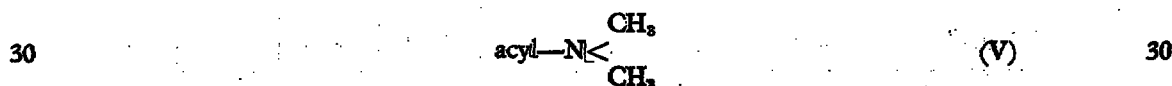
WHAT WE CLAIM IS:—

- 20 1. Insecticidal and acaricidal formulations containing as active compound O,O- 20
diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester of the formula

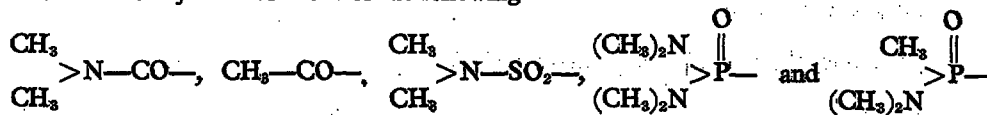


(I)

- the formulation containing
(1) 20 to 80% by weight of the active compound,
(2) 15 to 80% by weight of inert, higher-boiling hydrocarbon, chlorinated hydrocarbon
25 and/or ester as diluent, and 25
(3) 0.1 to 10% by weight of tertiary amine and/or 0.01 to 10% by weight of stable
dipolar aprotic solvent.
2. Formulations according to claim 1 in which the dipolar aprotic solvent is
dimethyl sulfoxide, N-methylpyrrolidone or a compound of the type



in which the acyl radical is one of the following



(VI)

3. Formulations according to claim 1 or 2 in which ingredient (2) is or includes
chlorobenzene, toluene, xylene, phosphoric acid O,O,O-triethyl ester or amyl acetate.
35 4. Formulations according to any of claims 1—3 in which ingredient (3) is or 35
includes triethylamine, pyridine, N-methylpiperidine, N,N-dimethyl-N-benzylamine,
collidine, dimethyl sulfoxide, N-methylpyrrolidone, tetramethyl urea, dimethyl-
acetamide, sulphuric acid bis-dimethylamide, phosphoric acid tris-dimethylamide and
methanephosphonic acid bis-dimethylamide.
40 5. Formulations according to any of claims 1—4 in which the proportion of 40
ingredient (3) is 1 to 8% by weight if tertiary amine and 0.1 to 7% by weight if
dipolar aprotic solvent.



6

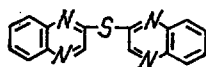
1,242,035

6

15

Comparative Example

Preparation of bis-[quinoxalyl-(2)]-sulphide by decomposition of O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester.



(III)

5

2580 g O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester were mixed with 10 ml of 50% acetic acid and allowed to stand for three days in a drying chamber at 60—70°C. Yellowish needles crystallised out. The decomposition mixture was kept at -10°C. for several hours, the liquid components were filtered off with suction and the solid residue was recrystallised from benzene-ligroin.

5

10

Yield: 792 g (62.5% of the theory)

10

bis-quinoxalyl-(2)-sulphide.

Melting point: 157—158°C.

Analysis:

Calculated for $C_{16}H_{10}N_4S$ (molecular weight 290.3)

15

	C	H	N	S
	66.18%;	3.48%;	19.30%;	11.05%;
Found:	66.21%;	3.91%;	19.04%;	11.01%;

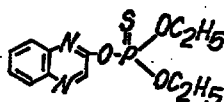
15

WHAT WE CLAIM IS:—

20

1. Insecticidal and acaricidal formulations containing as active compound O,O-diethyl-O-[quinoxalyl-(2)]-thionophosphoric acid ester of the formula

20



(I)

the formulation containing

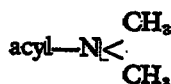
25

- (1) 20 to 80% by weight of the active compound,
- (2) 15 to 80% by weight of inert, higher-boiling hydrocarbon, chlorinated hydrocarbon and/or ester as diluent, and
- (3) 0.1 to 10% by weight of tertiary amine and/or 0.01 to 10% by weight of stable dipolar aprotic solvent.

25

2. Formulations according to claim 1 in which the dipolar aprotic solvent is dimethyl sulphoxide, N-methylpyrrolidone or a compound of the type

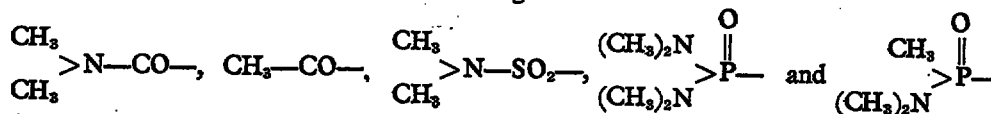
30



(V)

30

in which the acyl radical is one of the following



(VI)

35

3. Formulations according to claim 1 or 2 in which ingredient (2) is or includes chlorobenzene, toluene, xylene, phosphoric acid O,O,O-triethyl ester or amyl acetate.

35

4. Formulations according to any of claims 1—3 in which ingredient (3) is or includes triethylamine, pyridine, N-methylpiperidine, N,N-dimethyl-N-benzylamine, collidine, dimethyl sulphoxide, N-methylpyrrolidone, tetramethyl urea, dimethylacetamide, sulphuric acid bis-dimethylamide, phosphoric acid tris-dimethylamide and methanephosphonic acid bis-dimethylamide.

40

5. Formulations according to any of claims 1—4 in which the proportion of ingredient (3) is 1 to 8% by weight if tertiary amine and 0.1 to 7% by weight if dipolar aprotic solvent.

40

6. Formulations according to claim 1 substantially as hereinbefore described in the Examples.

7. A method of preparing a formulation according to any of claims 1—6 in which ingredient (1) is mixed with ingredients (2) and (3).

5 8. Formulations according to claim 1 whenever prepared by a method according to claim 7. 5

9. A method of combating insect or acarid pests which comprises applying to the pest or a pest habitat a formulation according to any of claims 1—6 or 8 alone or diluted with a solid or liquid diluent or carrier.

10 10. Crops protected from damage by insects or acarids by being grown in areas in which, immediately prior to and/or during the time of the growing, a formulation according to any of claims 1—6 or 8 is applied alone or in admixture with a solid or liquid diluent or carrier. 10

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings, Chancery Lane, London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

