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(54) PREPARATION HAVING A DEPOT GAS ACTION

(71) We, 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 insecticidal preparations, having a depot gas action, based on O,O-dimethyl-O1(2,2-dichlorovinyl)-thionophosphate as a gassing agent which acts automatically via the gas phase. The use of dimethyl-2,2-dichlorovinyl phosphate (DDVP) in formulations which automatically act as gassing agents, in combating pests, has been known for a long time. Very diverse materials have been proposed as carried for the above-mentioned active compound: macromolecular thermoplastic, thermosetting and elastomeric plastics or natural materials, such as wood, cardboard, asbestos, lime, gypsum, beeswax and montan wax. Further examples of suitable carriers are natural and synthetic rubber, polyolefins such as polyethylene, polypropylene and copolymers of ethylene and propylene, polyacrylates and copolyacrylates of methyl acrylate, ethyl acrylate and methyl methacrylate, polyvinyl compounds such as polystyrene, polyvinyltoluene and polyvinyl acetate, polyvinyl halides and polyvinylidene halides such as polyvinyl chloride, polyvinyl fluoride and polyvinylidene chloride, polyvinyl acetals such as polyvinyl butyral, linear and branched polyesters and polyethers, and cellulose plastics such as cellulose acetate, cellulose propionate, cellulose butyrate and cellulose nitrate. Examples of further suitable carriers are unsaturated polyesters, epoxides, polyurethanes, phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins.

The polymers and copolymers of vinyl chloride (see DT-AS (German Published Specification) 1,230,259) as well as unsaturated polyester systems (see DT-AS (German

Published Specification) 1,694,240 and DT-OS (German Published Specification) 2,231,099) have been described as particularly preferred carriers, as have also polymeric acrylates and polymeric vinyl compounds such as polystyrene.

In addition to the active compound, the formulations frequently also contain auxiliaries such as plasticisers, stabilisers, vaporisation regulators and fillers, depending on the nature of the carrier. Examples of possible plasticisers are dioctyl phthalate, alkane-sulphonic acid aryl esters, trioctyl phosphate, triphenyl phosphate, dibutyl adipate, chlorinated paraffin, diisononyl phthalate, di-2-ethylhexyl adipate, di-2-ethylhexyl phthalate and di-2-ethylhexyl sebacate. Examples of suitable stabilisers are phenols, amines or lower nitrogen-containing heterocyclic compounds, as well as azo and hydrazo compounds, acid anhydrides, epoxides and elementary sulphur (DT-OS (German Published Specification) 2,145,318), and also compounds which are usually employed for stabilising macromolecular substances, such as, for example, organic cadmium compounds and lead compounds as heat stabilisers for polyvinyl chloride.

Examples of suitable vaporisation regulators are palmitic acid ethyl ester, myristic acid isopropyl ester, di-n-butyl phthalate, 2-chloronaphthalene, camphor, benzoic acid, biphenyl, isobutyl benzoate and others, such as are described, for example, in East German Patent Specification 91,898 and also in DT-OS's (German Published Specifications) 1,954,501, 2,026,119 and 2,028,226.

Fillers may be, for example, fibres of glass, sisal, hemp, nettle, coir and flax, as well as titanium dioxide, iron oxides, kaolin, quartz and other inert materials.

The formulations in question are in most cases employed as mouldings such as slabs, sheets, tapes, bars, spheres, foams, strips, film, tablets or granules. If, in the course of use, such a moulding is, for example, brought into the living room or bedroom of

a house, or placed, in the form of a neck-band, round the neck of a domestic animal, the DDVP contained in the preparation is gradually released into the surrounding air, as a result of the vapour pressure of the DDVP or with the aid of heat sources, for example electrical energy, and thus automatically kills, via the gas phase, the pests present in the room and on domestic animals (see DT-AS (German Published Specification) 1,230,259; British Patent Specification 1,015,933; South African Patent Specification 62/371; DT-AS (German Published Specification) 1,694,240; DT-OS's (German Published Specifications) 1,941,046 and 2,231,099; and DT-AS (German Published Specification) 1,802,684).

The mouldings can either be employed for use directly or be surrounded by casings (quivers), which can be opened or closed completely or partially in order thereby periodically to interrupt the release of the DDVP or to regulate the amount of active compound released.

Now the problem of using DDVP in these automatic gassing mouldings is that the release of the active compound must be so controlled that sufficient active compound is released into the air of the room to kill the pests reliably whilst the humans and domestic animals present in the room are not harmed. Active compounds having a lower toxicity to mammals than has DDVP would therefore represent a great technical advance for this end use.

Though, in addition to DDVP, South African Patent Specification 62/371 describes combinations with a large number of other phosphoric acid esters and the corresponding thiophosphates, hitherto no other

compound than DDVP has attained practical importance in this respect. With regard to the thiophosphates, DT-AS (German Published Specification) 1,230,259 discloses that they are less compatible with macromolecular substances that are the phosphoric acid esters in question. Furthermore, it is generally known that thiophosphoric acid esters have a lower insecticidal power than the corresponding phosphates. The poorer insecticidal action of O,O-dimethyl-O-(2,2-dichlorovinyl)-thionophosphate (hereafter referred to for brevity as thio-DDVP) compared to DDVP is shown by the following comparison experiment:

Aerosol test

Test animals : *Musca domestica*
Solvent : Acetone

To produce a suitable preparation of active compound, the active compound was mixed, at a range of concentrations, with the stated solvent.

A wire cage which contained about 25 test animals was suspended in the centre of a gas-tight glass chamber of size 1 m³. After the chamber had been closed again, 2 ml of the preparation of active compound were atomised in the chamber. The condition of the test animals was constantly checked from outside, through the glass walls, and the time required for a knock-down effect on 50% of the animals was determined.

The active compounds, amounts used and time after which 50% of the animals were lying on their backs (LT₅₀) can be seen from the table which follows:

TABLE I
Aerosol test
Amount used
mg/m³

Active compound	Amount used mg/m ³	LT ₅₀
DDVP	1	10'37"
Thio-DDVP	1	19'15"
	2	13'37"
	3	11'40"
	4	9'20"

It is therefore not surprising that the above-mentioned publications do not contain an example of the use of thio-DDVP, or that this active compound is not mentioned anywhere therein, even cursorily, as an example in a list.

The present invention now provides an insecticidal preparation having a depot gas action, which preparation comprises O,O-

dimethyl - O - (2,2 - dichlorovinyl) - thionophosphate as a gassing agent, in admixture with an unsaturated polyester copolymer resin as a solid carrier.

Thio-DDVP has been found to be surprisingly effective when used in such preparations.

The invention also provides a method of combating insects which comprises expos-

ing the insects or their habitat to O,O-dimethyl - O - (2,2 - dichlorovinyl) - thionophosphate emitted as a gas from a preparation according to this invention.

In addition to the active compound, the preparations in question can also contain one or more of the above-mentioned auxiliaries or fillers, such as plasticisers, stabilisers, vaporisation regulators, vaporisation inhibitors, vaporisation promoters, glass fibres, textile fibres, pigments, dyestuffs, scents and quartz. The preparations may be used in the form of shaped articles such as slabs, sheets,

tapes, bars, spheres, foams, strips, films, tablets, neckbands or granules. They can be surrounded by casings which permit a controllable full or reduced release of active compound. A factor which proves particularly advantageous in the use, according to the invention, of thio-DDVP is that compared to DDVP the active compound, and its degradation products, decomposition products and possible by-products have a lower toxicity to warm-blooded animals, as can be seen from the table which follows:

TABLE 2

			LD ₅₀ male rats	
			DDVP	Thio-DDVP
30	Acute oral toxicity	...	62 mg/kg	773 mg/kg
			LD ₅₀ male rats	
35	Acute inhalation toxicity	...	DDVP	340 mg/m ³
	(4 hours' exposure)	...	Thio-DDVP	>477 mg/m ³ *
40	* This concentration, which is the maximum possible in the experiment, was tolerated without symptoms by the animals.			

The preparations according to the invention, based on thio-DDVP as an automatically acting gassing agent, and solid carriers, can be used to combat a great diversity of species of pests. The thio-DDVP to be used as the active compound according to the invention is known from the literature and can be prepared, for example, in accordance with the process described in DT-OS (German Published Specification) 2,238,921.

The following examples explain the invention in more detail, with "parts" denoting parts by weight.

For Examples 1 and 2, the carrier used was in each case a mixture of 440 parts of an unsaturated polyester (prepared by polycondensation of 205.8 parts of maleic anhydride, 725.2 parts of phthalic anhydride, 546.4 parts of 1,2-propanediol and 0.265 parts of hydroquinone, and having an acid number of 42) and 240 parts of styrene (polyester mixture 1).

For Examples 3 and 4, the carrier used was in each case a mixture of 730 parts of an unsaturated polyester (prepared by polycondensation of 262.8 parts of maleic anhydride, 926.8 parts of phthalic anhydride, 612 parts of 1,2-propanediol, 359.6 parts of dipropylene glycol and 0.214 parts of hydroquinone, and having an acid number of 3.9) and 350 parts of styrene (polyester mixture 2).

EXAMPLE 1

A homogeneous premix was prepared

from 680 parts of polyester mixture 1, 390 parts of thio-DDVP, 230 parts of alkane-sulphonic acid aryl ester and 27 parts of maleic anhydride. After adding 41 parts of a 10% strength solution of dimethylaniline in toluene, a cast sheet having a glass fibre content of 26% was produced by heating the mixture for about 30 minutes to 80—100°C in a closed mould in which a glass fibre mat (600 g/m²) had been laid. The sheet was subsequently cut into shaped pieces of size 8×25 cm. The active compound content was 20 g.

EXAMPLE 1a

(Comparison Example)

Shaped pieces of size 8×25 cm and having an active compound content of 29 g were produced in the same manner as described in Example 1, but using DDVP as the active compound.

EXAMPLE 2

A homogeneous premix was prepared from 630 parts of polyester mixture 1 and 450 parts of thio-DDVP. After adding 36 parts of benzoyl peroxide in phthalate plasticiser (50% strength), a cast sheet having an asbestos content of 3.5 per cent by weight was produced by heating for about 30 minutes to 80—100°C in a closed mould, into which granular asbestos particles had been introduced. The sheet was subsequently cut into shaped pieces of size 8×25 cm, having an active compound content of 38%.

1.8

EXAMPLE 3

A homogeneous premix was prepared from 665 parts of polyester mixture 2 and 475 parts of hio-DDVP. After adding 38 parts of benzoyl peroxide in phthalate plasticiser (50% strength), a cast sheet with a fabric content of 26 per cent by weight was produced by heating for about 30 minutes to 80—100°C in a closed mould, into which a fabric of polyacrylonitrile fibres (280 g/m²) has been laid. The sheet was subsequently cut into shaped pieces of size 8×25 cm, having an active compound content of 24 g each.

EXAMPLE 3a

(Comparison Example)

A homogeneous premix, and shaped pieces of the same sizes and of the same active compound content, were prepared in the same manner as in Example 3, but using DDVP as the active compound.

EXAMPLE 4

A homogeneous premix was prepared from 438 parts of polyester mixture 2 and 299 parts of thio-DDVP. After adding 26 parts of benzoyl peroxide in phthalate plasticiser (50% strength), a cast sheet with a weight content of 26 per cent by weight was produced by heating for about 30 minutes to 80—100°C in a closed mould, into which a jute fabric (1,150 g/m²) had been laid. The sheet was subsequently cut into shaped pieces of size 8×25 cm, having an active compound content of 25 g each.

EXAMPLE 4a

(Comparison Example)

A homogeneous premix, and shaped pieces

of the same sizes and of the same active compound content, were prepared in the same manner as in Example 4, but using DDVP as the active compound.

EXAMPLE A

One shaped piece produced according to Example 1 and one shaped piece produced according to Example 1a were each pushed into a casing of fine wire mesh and suspended from the ceiling in the centre of identical rooms of 50 m³ cubic capacity. Four weeks later, 200 flies of the species *Musca domestica* were released in the rooms. In the room in which the shaped piece according to Example 1 was suspended, the flies dropped after 2 hours. In the room in which the shaped piece according to Example 1a was suspended, it required 3 hours for 100% of the flies to lie on their backs.

EXAMPLE B

On shaped piece produced according to Example 3 and one shaped piece produced according to Example 3a were each pushed into a net-like quiver and suspended from the ceiling in the centre of identical rooms of 40 m³ cubic capacity. Immediately thereafter (0), and after 4, 8 and 12 weeks, 200 flies of the species *Musca domestica* were in each case exposed in the rooms. The flies did not come into direct contact with the shaped pieces. In each case, the percentage of animals which had fallen on their backs was determined 1 hour after exposing the flies. The results obtained can be seen from the table which follows:

TABLE 3

Age of the shaped pieces, in weeks	Percentage of animals lying on their backs after one hour	
	DDVP	Thio-DDVP
0	80	100
4	70	95
8	60	90
12	20	50

EXAMPLE C

One shaped piece produced according to Example 4 and one shaped piece produced according to Example 4a were each pushed into an open-pore quiver and suspended open in a room. After 2 weeks, the shaped piece according to Example 4 was first brought

into a room of 43 m³ cubic capacity and 300 flies of the species *Musca domestica* were released. The time after which 100% of the flies had fallen on their backs was determined. Thereafter the room was thoroughly aired and the same experiment was carried out with the shaped piece according to Ex-

ample 4a. The results obtained are shown in the following table:

TABLE 4

	Shaped piece according to Example	Time elapsed before 100% of the animals were lying on their backs (hours)
10	4	2
	4a	5

WHAT WE CLAIM IS:—

- 15 1. An insecticidal preparation having a depot gas action, which preparation comprises O,O-dimethyl-O-(2,2-dichlorovinyl)-thionophosphate as a gassing agent, in admixture with an unsaturated polyester co-
- 20 polymer resin as a solid carrier.

2. A preparation according to claim 1, which also comprises one or more auxiliaries or fillers selected from plasticisers, stabilisers, vaporisation promoters, vaporisation in-

hibitors, glass fibres, textile fibres, pigments, 25 dyestuffs, scents and quartz.

3. A preparation according to claim 1 or 2, contained in a casing which adjustably provides for full or reduced release of the gassing agent. 30

4. A preparation according to claim 1, substantially as hereinbefore described in any one of Examples 1 to 4.

5. A method of combating insects which comprises exposing the insects or their 35 habitat to O,O-dimethyl-O-(2,2-dichlorovinyl)-thionophosphate emitted as a gas from a preparation according to any of claims 1 to 4.

6. A method according to claim 5, in 40 which the insects are flies.

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