

[54] **INSECTICIDAL COMPOSITION
EMPLOYING DDVP**

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[22] Filed: **Oct. 5, 1972**

[21] Appl. No.: **295,272**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 37,571, May 15,
1970, abandoned.

Foreign Application Priority Data

Feb. 12, 1970 United Kingdom..... 26970/69

[52] U.S. Cl. **424/19; 424/219; 424/353**

[51] Int. Cl. **A01n 9/36; A01n 17/00**

[58] **Field of Search** 424/19, 219, 357, 353

[56] **References Cited**

UNITED STATES PATENTS

3,364,105 1/1968 Geiger et al. 424/357

FOREIGN PATENTS OR APPLICATIONS

1,010,191 11/1965 United Kingdom

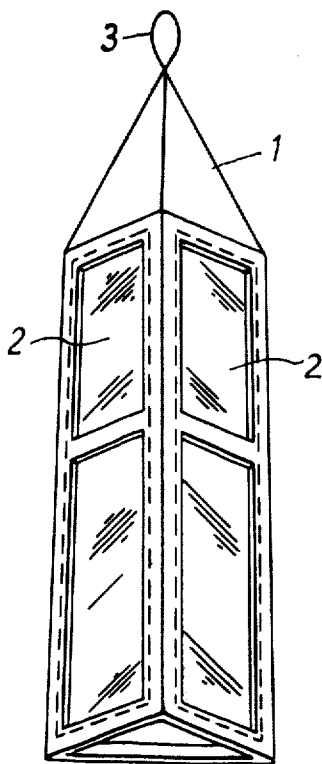
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[57] **ABSTRACT**

The present application relates to insecticidal materials containing 2,2 dichlorovinyl dimethyl phosphate and paradichlorobenzene.

1 Claim, 1 Drawing Figure



INSECTICIDAL COMPOSITION EMPLOYING DDVP

This is a continuation-in-part of application Ser. No. 37,571, filed May 15, 1970, now abandoned.

THE PRIOR ART

Insecticidal compositions are known which are functional as general insect poisons on contact, by ingestion or by inhalation and have been widely used as sprays, dusts or baits. Insecticides such as 2,2 dichlorovinyl dimethyl phosphate (hereinafter referred to as DDVP) are known for use in such compositions. DDVP has a relatively high vapour pressure and whilst generally stable under dry conditions readily hydrolyses when in contact with moisture. In view of these properties, which are disadvantageous in the use of this compound as an insecticide, various different forms of compositions containing DDVP have been proposed to enable it to be effectively dispensed. Thus it has been proposed to impregnate solid insert carrier materials such as cork, paper, wood, sawdust, cotton, vermiculite, clays or porous ceramics with compositions containing DDVP in order to increase its effective life of persistence and ability to be released to the surrounding atmosphere at a controlled rate. It has been found however that the use of such carrier materials tended to shorten the effective life of the compound and that also the carrier materials contained traces of water difficult to remove or absorbed moisture from the atmosphere, resulting in the degradation of the DDVP generally thought to be due to hydrolysis.

It is also known from British Patent Specification No. 1,010,191 (Sheel Internationale Research Maatschappij N.V.) to provide a solid insecticidal composition comprising paradichlorobenzene in which has been incorporated up to 10 percent of 2,2 dichlorovinyl dimethyl phosphate. In respect of this composition however it has been found that although providing acceptable insecticidal activity the activity is not maintained for a length of time necessary for a commercially viable product.

It is an object of the present invention to provide an insecticidal material which substantially overcomes any of the aforesaid disadvantages. Other objects of the invention will become apparent from the description hereafter.

SUMMARY OF THE INVENTION

According to the present invention there is provided an insecticidal material comprising a porous ceramic carrier impregnated with a liquid mixture of a 2,2 dichlorovinyl dimethyl phosphate (DDVP) and from about 5 to 20 percent by weight of paradichlorobenzene based on the total weight of the mixture.

Paradichlorobenzene is itself well known as an insecticide for example as a moth repellent and killer, consequently when used in the material of the present invention the combined insecticidal properties are exhibited, whilst the hydrophobic nature of the PDCB protects the DDVP from attack by moisture. Thus in the form of a liquid mixture absorbed upon the ceramic carrier it is found that the PDCB acts as a "waterproofing agent" for the DDVP preventing hydrolysis in the presence of moisture whilst at the same time, since it itself is volatile, allowing the DDVP vapour to emerge from the carrier in a controlled manner. In this form the in-

secticidal material of the present invention finds application in domestic surroundings, in industrial premises, greenhouses, warehouses and storage places for food-stuffs, grains, cereals, etc.

The ceramic carrier may be a ceramic body preferably in the form of a plate. In practice these porous ceramic plates impregnated with the liquid mixture may be marketed in a vapour-proof package e.g. a heat sealed laminate of tinfoil and polythene and when required for use may be hung by a cord threaded through a hole in the material or be mounted in a suitable device or holder for example a lantern of the design illustrated in the accompanying drawing which shows a perspective view of a lantern of attractive design constructed to hold these rectangular ceramic plates.

Referring to the drawing a triangular lantern which may be fabricated of say carboard and which may be folded flat when not in use carries three ceramic plates 2 one adjacent to each side of the lantern. A loop 3 of string or other suitable material is provided at the top of the lantern for carrying or suspending in a suitable position. The purpose of the lantern device is to present an adequate and predetermined area of surface to enable the volatilisation of the insecticidal composition to take place at a rate suitable to the conditions under which it is to be employed.

THE SPECIFIC EMBODIMENTS

The present invention is illustrated with reference to the following examples:

EXAMPLE 1.

A lantern such as that described above with reference to the drawing consists of three ceramic plates of convenient size, e.g. $16 \times 5.5 \times 0.3$ cm. suspended in a triangular card frame. Each plate is impregnated to an extent of 23.2 percent of its dry weight with a liquid mixture 80 parts by weight of DDVP and 20 parts by weight of PDCB which is slowly vaporised on exposure to the air.

The lantern was hung from the centre of the ceiling of a 1,000 ft. 3 empty test room which remained closed and unventilated except when entered twice a week to check conditions or when fly tests were carried out. The temperature was maintained at 21°C (70°F) and the relative humidity at $50\% \pm 5\%$.

Tests with Standard Reference Strain house flies were carried out after 1 week and then at two weekly intervals until the ninth week and weekly intervals from then until the twelfth week. About 200 flies were released into the treatment room and knock downs noted until complete. The results are given in the table. Very satisfactory results were still obtained even after twelve weeks.

Percentage Knock Down of Flies (about 200 used)
Weekly Observation Times 30 (minutes)

1	100
3	100
5	100
7	100
9	100
11	100
12	100

EXAMPLE 2

In order to demonstrate fully the surprising advantage of the invention the following samples were prepared and tested;

i. Sample A — a solid composition according to the British Pat. No. 1,010,191 (Shell) and consisting essentially of a mixture of 10 parts by weight of DDVP and 90 parts by weight of PDCB cast as a block having the dimensions 16.2 cm. $\times$ 5.4 cm. $\times$ 0.40 cm.

ii. Sample B — a ceramic tile of dimensions 16.2 cm. $\times$ 5.4 cm. $\times$ 0.35 cm., that is equal in dimensions and therefore in initial surface area to the cast block of Sample A impregnated to an extent of 23.2 percent of its dry weight with a liquid mixture of 80 parts by weight DDVP and 20 parts by weight of PDCB that is a composition according to the invention.

The samples were subjected to the following tests;

i. Cumulative weight loss test. Each sample was suspended from the ceiling of a 260 ft³ room. The ceramic tiles were suspended by a thread through a small drilled hole, the cast block of Sample A was held in a nylon net sling.

The rooms were empty, unventilated and identical in shape. The temperature was maintained at a constant 70°F (21°C), the humidity was uncontrolled and was in the range 50–60% during the 30 day test period.

Each device was weighed at intervals of 1–4 days. The weight losses are given in Table I. Vaporiser A evaporated to nothing between the 9th and 11th day.

ii. Air sampling and dichlorves estimation. The atmosphere was sampled by passing 76 litres of air at the rate of 3.8 l per minute, through deionised water using an air pump and sintered glass bubbler. The aqueous solution so obtained was immediately extracted with 3 $\times$ 15 ml. of redistilled hexane. The aqueous layer was discarded and the hexane extracts combined and made up to 50 ml. with hexane. 5 ml. aliquots equivalent to 7 ml. of air were injected onto a gas liquid chromatograph. Instrument used was a Perkin Elmer F11 fitted with an electron capture detector. The column was 3ft. $\times$ $\frac{1}{4}$ inch o.d. glass packed with 10% phenyl-diethanolamine succinate of Chromosorb W, 100–120 mesh. The operating conditions were as follows:

Oven temperature 140°C. Detector temperature 205°C.

Injection block temperature 195°C.

Carrier gas nitrogen at 50 ml/min. The DDVP concentrations in the air are shown in Table II.

TABLE I

Day	Weight losses of Vaporisers (grams)			
	A		B	
	DDVP in PDCB		DDVP + PDCB in Ceramic	
	Weight	Loss	Weight	Loss
0	48.194		60.329	
1	40.926	7.268	58.532	1.797
2	32.248	8.578	58.155	.377
3	25.076	7.272	58.014	.141
4	18.568	6.508	57.919	.095
7	8.279	10.289	57.568	.351
9	3.577	4.702	57.232	.336
11	0	3.577	56.998	.234
14			56.554	.444
17			56.072	.482
21			55.587	.485
24			55.165	.422
29			54.525	.640
31			54.275	.250
Total weight loss				6.054

TABLE II

Vaporiser	Dichlorves air concentrations in ug/litre.	
	A	B
2 days	0.7	
7 days	0.38	
15 days		0.5
23 days		0.16

The results in Table I show that Sample A according to the British Patent Specification No. 1,010,191 has completely evaporated. In contrast sample B however still contains an active DDVP content at 31 days.

The results in Table II show that Sample A, consistent with its complete evaporation in 10 days as shown in Table I does not give any DDVP concentration in the atmosphere after 10 days; but sample B also consistent with the results shown in Table I shows continued active DDVP concentration in the atmosphere with no indication of imminent complete expiry.

From these results therefore it is clear that the compounding of PDCB with DDVP in certain proportions according to the invention retards the degradation of DDVP by hydrolysis, preserving a concentration of DDVP vapour sufficient to give a 100 percent Knock-down of Flies in 80 minutes at the 12th week of exposure (see Example 1).

EXAMPLE 3

The following tests were carried out with insecticidal materials according to the invention using liquid mixtures of differing proportions of DDVP and PDCB.

Weight loss determinations were carried out on standard ceramic tiles impregnated in accordance with the invention with a solution of DDVP containing varying amounts of PDCB. To accelerate the weight loss the determination was made in a standard 1,000 cu. ft. chamber at a temperature of 80°F as opposed to previous determinations of 70°F. In other respects the tests were carried out as in Example 2 (Table I).

Sample D — a standard ceramic tile size 16.2 cm. long, 5.4 cm. wide and 0.35 cm. thick impregnated to an extent of 23.2 percent of its dry weight with a liquid mixture of 95 parts by weight of DDVP and 5 parts by weight of PDCB.

Sample E — a standard ceramic tile size 16.2 cm. $\times$ 5.4 cm. $\times$ 0.35 cm. impregnated as with Sample D but using a liquid mixture of 90 parts by weight of DDVP and 10 parts by weight of PDCB.

Sample F — a standard ceramic tile size 16.2 cm. $\times$ 5.4 cm. $\times$ 0.35 cm. impregnated as with Sample D but using a liquid mixture of 85 parts by weight DDVP and 15 parts by weight PDCB. The results obtained and shown in Table III below indicate that the weight loss performance in each case is very similar to that of Sample B referred to in Example 2.

TABLE III

TIME (Hours)	Weight loss of vaporiser (grams)		
	Sample D	Sample E	Sample F
0	62.62	58.67	60.51
5	62.12	57.84	59.26
30	61.28	56.83	58.11
70	60.24	55.87	57.13
101	59.54	55.13	56.37
125	59.40	54.70	55.87
149	58.62	54.23	55.39
173	58.23	53.87	55.04

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I claim:

1. An insecticidal material comprising a porous ceramic carrier impregnated with at least an insecticidal amount of a liquid mixture of 2,2 dichlorovinyl dimethyl phosphate and from about 5 to about 20 per-

cent by weight of paradichlorobenzene based on the total weight of the mixture, the porosity of said ceramic carrier being sufficient to allow absorption thereby of an insecticidal amount of the liquid mixture.

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