

PATENT SPECIFICATION

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(54) INSECTICIDAL COMPOSITIONS

(71) We, ROUSSEL UCLAF, a French Body Corporate, of 35 Boulevard des Invalides, Paris 7e, France, 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 novel insecticidal fumigating compositions.

As is known, allethrin and pyrethrin are both widely used as insecticides. From amongst the eight isomers of allethrin it has been found that d-2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl d-*trans* chrysanthemate, (i.e., d-allethrolone d-*trans*-chrysanthemate, has the highest insecticidal activity [W. A. GERSDORFF and N. MITILIN, J. Econ. Entomol., 46, page 999 (1953)]. However, as emphasised in 1970 in French Patent No. 2,067,303, the production of d-allethrolone and its subsequent conversion into the d-*trans*-chrysanthemate was not at that time, regarded as feasible on a commercial scale.

Accordingly, commercial interest was directed to the dl-allethrolone d-*trans*-chrysanthemate isomer which was more accessible and which had shown a more interesting activity when used in the form of fumigating agents.

We have since discovered a process for resolving dl-allethrolone whereby d-allethrolone can be produced on an industrial scale and in an advantageous manner, the said process being described and claimed in our copending Application No. 59882/72 (Serial No. 1,401,350).

We have now found that d-allethrolone d-*trans*-chrysanthemate has an unexpectedly advantageous activity compared with that of dl-allethrolone d-*trans*-chrysanthemate when used in the form of a fumigating agent.

According to one feature of the present invention we provide insecticidal fumigating compositions of the type referred to comprising, as active ingredient, d-allethrolone d-

trans-chrysanthemate together with a suitable carrier as herein defined.

The expression "insecticidal fumigating compositions of the type referred to" is used herein to denote insecticidal compositions which, when subjected to heating, combustion or atomisation, effect release of the active ingredient, e.g. by diffusion, vaporisation, atomisation, formation of a smoke, etc. into the ambient atmosphere. The carrier used together with the active ingredient must of course be one suitable for the intended purpose and thus the expression "suitable carrier" as used herein means a carrier (or mixture of carriers) suitable for the formulation of fumigating compositions of the type referred to.

The new fumigating compositions according to the present invention have been found to have a good "knock-down effect" which renders them useful as sanitary, agricultural and horticultural insecticides. The expression "knock-down effect" is used herein to denote the action of the compound in rapidly immobilising the insects even though the insects may not all be killed.

One would expect that in the most favourable conditions, i.e. assuming that 1-allethrolone d-*trans*-chrysanthemate is totally devoid of activity, the ratio of insecticidal activity between d-allethrolone d-*trans*-chrysanthemate and dl-allethrolone d-*trans*-chrysanthemate would be 2:1.

However, in tests on mosquitos using d-allethrolone d-*trans*-chrysanthemate and dl-allethrolone d-*trans*-chrysanthemate in the form of fumigating compositions, we have found that the knock-down activity ratio between these two compounds is about 3:1. These results suggest the possibility of some unforeseen anti-synergistic phenomenon wherein the presence of 1-allethrolone inhibits the total activity of the racemic mixture. Thus, when used in the form of fumigating compositions, d - allethrolone d - *trans* - chrysanthemate is thus the allethrin isomer having

[Price 33p]

Price 75p

the best insecticidal effectiveness in terms of "knock-down" effect.

In general, the compositions according to the invention preferably contain from 0.05 to 95% by weight of the active ingredient.

The compositions according to the present invention can be prepared for example in the form of an insecticidal spiral or coil, preferably containing 0.05 to 10% by weight of d-allethrolone d-*trans*-chrysanthemate as active ingredient, together with a combustible support composed for example of pyrethrum residue, Tabu powder (powder of *Machilus Thumbergia* leaves), pyrethrum stalk powder, cedar leaf powder, wood powder (such as pine sawdust), starch and coconut shell powder.

The compositions according to the invention can also be obtained by incorporating the d-allethrolone d-*trans*-chrysanthemate, preferably in a concentration of 0.05 to 95% by weight, in an incombustible fibrous substrate and placing the fumigating composition thus obtained on a heating apparatus, for example an apparatus known as an electric mosquito destroyer, serving to vaporise the active constituent whereby the vaporisation of the active ingredient can be controlled as desired.

Alternatively the compositions according to the invention can comprise an atomisable oil, preferably containing from 0.05 to 95% by weight of d-allethrolone d-*trans*-chrysanthemate, which can be used to impregnate the mesh of a lamp to effect combustion of the oil and vaporisation of the active constituent.

The compositions according to the present invention can also include, if desired, products which act as stabilisers, such as phenols or arylamines, and/or conventional synergistic pyrethrinoid compounds such as N-(2-ethylhexyl)-bicyclo (2,2,1) hepta-5-ene anhydrophthalic acid 2,3-dicarboximide or α [2 - (2 - butoxyethoxy) - ethoxy] - 4,5-methylenedioxy - 2 - propyltoluene (or piperonyl butoxide). These compositions may also contain colouring agents such as Malachite green.

The compositions according to the invention may be used in dwellings for destroying insects such as flies, mosquitos, etc., and on industrial premises for destroying for example insects harmful to cereals and horticulture.

According to a further feature of the present invention we provide a method which comprises treating a fumigating composition

according to the invention to effect release of an insecticidally effective amount of the active ingredient in or on a site containing, or liable to contain, insects, e.g. mosquitos.

This, for example, in the above-described method according to the present invention, the fumigating composition may be heated or ignited, e.g. in a lamp, to effect vaporisation of the active ingredient.

The d-allethrolone d-*trans*-chrysanthemate employed in the compositions according to the invention can be obtained for example by reacting d-*trans*-chrysanthemic acid (or a functional derivative thereof) with d-allethrolone or an alkali metal derivative thereof, e.g. by reacting d-*trans*-chrysanthemic acid chloride with d-allethrolone in the presence of a tertiary base such as pyridine, as described in the Preparation given hereinafter.

The following Examples illustrate the present invention.

Example 1.

Comparative study of the insecticidal activity on *Aedes aegypti* of d-allethrolone d-*trans*-chrysanthemate (compound A) and d-allethrolone d-*trans*-chrysanthemate (compound B) used in the form of fumigation agent.

A) *Smoke-producing spiral technique (coil)*. The test is carried out in a cubic aerosol chamber with a side of 3 m, i.e. a volume of 27 m³.

The adult *Aedes aegypti* are placed in plastic cylindrical boxes having a diameter of 10 cms and a height of 3 cms, the two ends of these boxes being closed by netting. About 25 adult *Aedes aegypti* as used per box, 4 boxes being used for each test, with 4 repetitions per test. The boxes are placed 60 cms from the ground at the four top corners of a square with a side of one metre. The axis of the boxes are arranged horizontally.

The active material is incorporated in spirals of inert material, the desired quantity of active ingredient being added to the inert material in an acetone solution using a pipette.

The spiral is placed at the centre of the aerosol chamber 10 cms from the ground.

The knock-down tests were carried out every two minutes following the start of combustion of the spiral and lasted a period of 30 minutes.

Table I summarises the experimental results obtained.

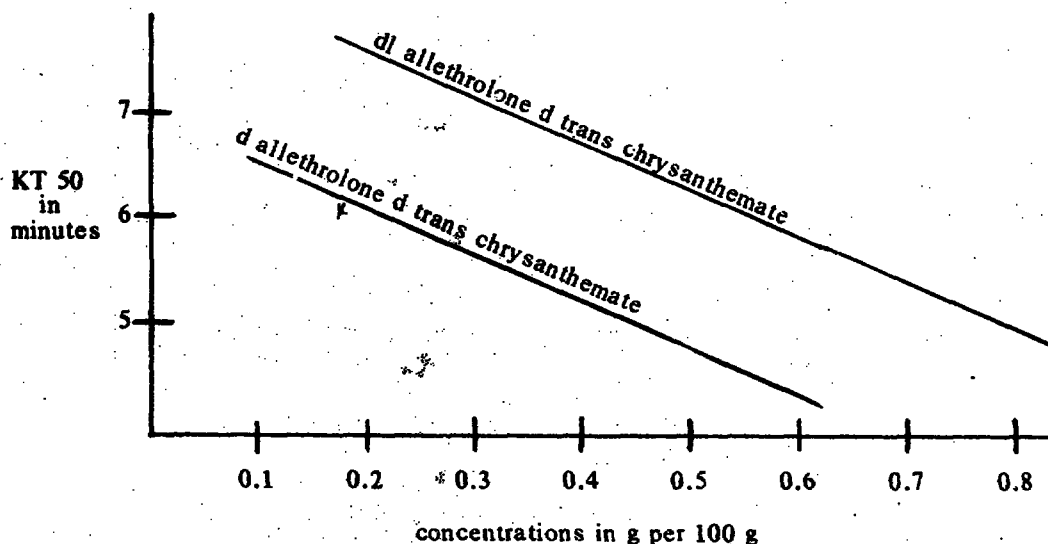
TABLE I

Activity with adult *Aedes aegypti*
(anti-mosquito spirals)

Products	Concentrations in g. per 100 g.	(*) KT 50 (minutes)	Relative strengths in terms of concentrations corresponding:			
			to 0.50% of compound B		to 0.75% of compound B	
			Concen- trations	Relative strengths	Concen- trations	Relative strengths
Compound B	0.75 0.50 0.25	5.8 6.5 7.5	0.50	1	0.75	1
Compound A	0.50 0.25 0.125	5.0 6.0 6.7	0.16	3.1	0.29	2.6

(*) The KT 50 or knock-down time 50 denotes the time necessary to knock down 50% of the insects with a determined dose of active material. This time is in inverse proportion to the rapidity of the action of the compound.

The results of Table I can be graphically represented in the following way:



B) "Mosquito destroyer" technique.

The technique used is analogous to the preceding one but the spiral is replaced by a small electrical apparatus containing a heating plate heated to a temperature of about 130° C. A small cardboard rectangle in which

the active material has been incorporated by applying an acetone solution thereof with a pipette, is deposited on the heating plate.

Table 2 summarises the experimental results obtained.

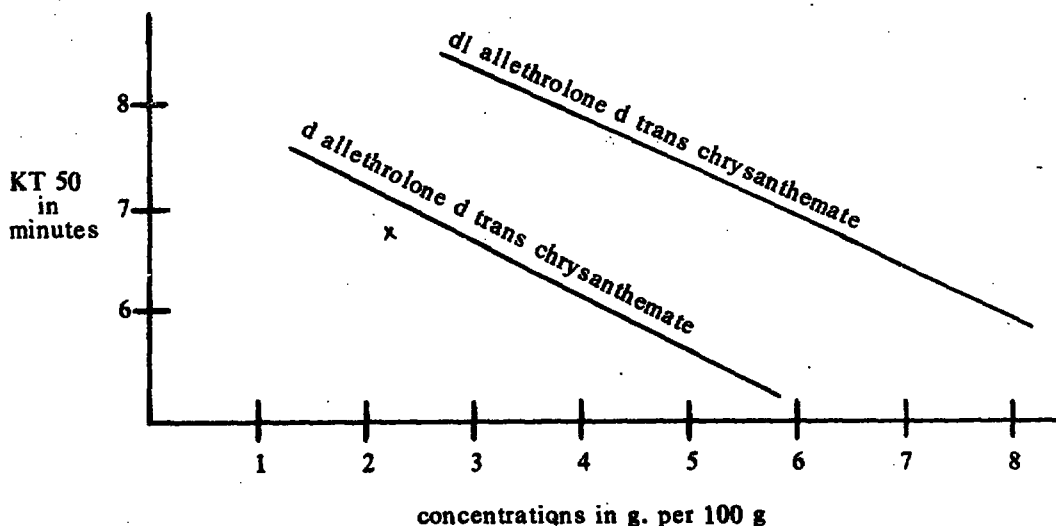
TABLE 2

Activity with adult *Aedes aegypti*

(electro mosquito destroyer)

Products	Concentrations in g. per 100 g.	KT 50 (minutes)	Relative strengths in terms of concentrations corresponding:			
			to 0.50% of compound B		to 0.75% of compound B	
			Concen- trations	Relative strengths	Concen- trations	Relative strengths
Compound B	7.5 5.0 2.5	6.5 7.1 8.2	5.0	1	7.5	1
Compound A	5.0 2.5 1.25	5.6 6.7 7.4	1.8	2.8	3.0	2.5

The results of Table 2 can be graphically represented in the following way:



C) Conclusion:

Tables 1 and 2 as well as the corresponding graphic representations show that the ratio of knock-down activities of d-allethrolone d-trans-chrysanthemate and dl-allethrolone d-trans-chrysanthemate lies between 2.6 and 3.1 for the smoke-producing spiral tests and between 2.5 and 2.8 for "mosquito destroyer" tests.

Example 2.

Preparation of a smoke-producing spiral. A solution of 0.4 g of d-allethrolone d-trans-chrysanthemate in 5 cc of methanol is carefully incorporated into a mixture made up of 30 g of pyrethrum residue, 12 g of pyrethrum stalk powder, 51.1 g of coconut shell powder, and 6 g of soluble starch. The resulting powder is mixed with about 100 g

of water, dried and made into a spiral about 0.4 cms in thickness and with a diameter of about 12 cms.

Example 3.

- 5 Preparation of a smoke-producing spiral.
A solution of 0.6 g of d-allethrolone d-*trans*-chrysanthemate in 5 cc of methanol is carefully incorporated into a mixture made up of 43 g of pyrethrum stalk powder, 52 g of coconut shell powder and 4.4 g of soluble starch. The resulting powder is mixed with about 100 g of water, dried and made into a spiral shape about 0.4 cms in thickness and with a diameter of about 12 cms.

Example 4.

- 15 Preparation of a composition intended to be heated electrically.
A solution of 0.6 g of d-allethrolone d-*trans*-chrysanthemate in 5 cc of toluene was adsorbed onto the surface of a parallelepipedal piece of asbestos with dimensions of $2 \times 2 \times 0.8$ cms. A second piece of asbestos with the same dimensions was fixed onto the first piece of asbestos to produce a smoke-producing composition which can be heated on an electrical resistant heating plate.

Preparation of d-allethrolone d-*trans*-chrysanthemate.

500 g of d-allethrolone

- 30 $[(\alpha)_D^{20} = +15^\circ$ ($c=1\%$ chloroform),
U.V. spectrum (ethanol = max. at 230 nm
($E_{1\%}^{1\text{cm}} = 806$) circular dichroism (dioxan)
inflection at 346.5 nm ($\Delta\epsilon = +1.30$) max. at 331 nm ($\Delta\epsilon = +2.89$) max. at 320 nm ($\Delta\epsilon = +3.28$) inflection at 310 nm ($\Delta\epsilon = +2.43$) max. at 230 nm ($\Delta\epsilon = -18.72$)]
was introduced under an inert atmosphere into 1,000 cc of benzene and 340 cc of pyridine at ambient temperature. 613 g of d-*trans*-chrysanthemic acid chloride [b.p.: 82°C under 6 mm of mercury, $[\alpha]_D^{20} = +12.4^\circ$ ($c=1\%$, pyridine containing 25% water)] in solution in 500 cc of benzene was added to the mixture which was agitated for 3 hours, poured into a dilute aqueous solution of hydrochloric acid and the benzene phase washed with a diluted aqueous solution of hydrochloric acid, with water until pH is bordering 7, then with an aqueous solution of sodium bicarbonate until pH = 8.5 and finally with water, the various aqueous washing agents being reextracted with benzene as they are obtained. The benzene phases are combined, dried on magnesium sulphate, 55 0.8 g of hydroquinone added, then some active charcoal, and the mixture agitated. The active charcoal and the sulphate were removed by filtration, 500 g of alumina added,

the mixture agitated, the alumina removed by filtration and the mixture concentrated to dryness by distillation, first under normal pressure, then under reduced pressure to obtain 940 g of d-allethrolone d-*trans*-chrysanthemate.

WHAT WE CLAIM IS:—

1. Insecticidal fumigating compositions of the type referred to comprising, as active ingredient, d-allethrolone d-*trans*-chrysanthemate together with a suitable carrier as herein defined.

2. Compositions as claimed in claim 1 containing 0.05 to 95% by weight of the active ingredient.

3. Compositions as claimed in claim 1 or claim 2 in a form whereby release of the active ingredient is effected by heating.

4. Compositions as claimed in any of the preceding claims wherein the said carrier comprises a combustible material.

5. Compositions as claimed in claim 4 wherein the combustible material comprises at least one of the following:— pyrethrum residue, Tabu powder, pyrethrum stalk powder, cedar leaf powder, wood powder, starch or coconut shell powder.

6. Compositions as claimed in claim 4 or claim 5 in the form of spirals or coils.

7. Compositions as claimed in any of claims 4 to 5 containing 0.05 to 10% by weight of the active ingredient.

8. Compositions as claimed in any of claims 1 to 3 wherein the said carrier comprises an incombustible fibrous substrate.

9. Compositions as claimed in any of claims 1 to 3 wherein the said carrier comprises an atomisable oil.

10. Compositions as claimed in any of the preceding claims further containing a stabiliser and/or a synergistic agent.

11. Compositions as claimed in claim 10 wherein the stabiliser comprises a phenol or arylamine.

12. Compositions as claimed in claim 10 or claim 11 wherein the synergistic agent comprises N-(2-ethylhexyl)-bicyclo-(2,2,1)-hepta-5-ene anhydrophthalic acid 2,3-dicarboximide or α -[2-(2-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyl-toluene.

13. Compositions as claimed in claim 1 substantially as herein described.

14. Insecticidal fumigating compositions as claimed in claim 1 substantially as herein described with reference to any of the Examples.

15. A method which comprises treating a fumigating composition as claimed in any of the preceding claims to effect release of an insecticidally effective amount of the active ingredient in or on a site containing, or liable to contain insects.

16. A method as claimed in claim 15 wherein the insects are mosquitos.

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of water, dried and made into a spiral about 0.4 cms in thickness and with a diameter of about 12 cms.

Example 3.

- 5 Preparation of a smoke-producing spiral.
A solution of 0.6 g of d-allethrolone d-*trans*-chrysanthemate in 5 cc of methanol is carefully incorporated into a mixture made up of 43 g of pyrethrum stalk powder, 52 g of coconut shell powder and 4.4 g of soluble starch. The resulting powder is mixed with about 100 g of water, dried and made into a spiral shape about 0.4 cms in thickness and with a diameter of about 12 cms.

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A solution of 0.6 g of d-allethrolone d-*trans*-chrysanthemate in 5 cc of toluene was adsorbed onto the surface of a parallelepipedal piece of asbestos with dimensions of 2 × 2 × 0.8 cms. A second piece of asbestos with the same dimensions was fixed onto the first piece of asbestos to produce a smoke-producing composition which can be heated on an electrical resistant heating plate.

Preparation of d-allethrolone d-*trans*-chrysanthemate.

500 g of d-allethrolone

- 30 $[(\alpha)_D^{20} = +15^\circ \text{ (c=1\% chloroform)},$
U.V. spectrum (ethanol=max. at 230 nm
($E_{1cm}^{1\%} = 806$) circular dichroism (dioxan)
inflection at 346.5 nm ($\Delta\epsilon = +1.30$) max.
at 331 nm ($\Delta\epsilon = +2.89$) max. at 320 nm
35 ($\Delta\epsilon = +3.28$) inflection at 310 nm
($\Delta\epsilon = +2.43$) max. at 230 nm ($\Delta\epsilon = -18.72$)]
was introduced under an inert atmosphere into 1,000 cc of benzene and 340 cc of pyridine at ambient temperature. 613 g of d-*trans*-chrysanthemic acid chloride [b.p.: 82° C under 6 mm of mercury,
40 $[\alpha]_D^{20} = +12.4^\circ \text{ (c=1\%, pyridine containing 25\% water)}$ in solution in 500 cc of benzene was added to the mixture which was agitated for 3 hours, poured into a dilute aqueous solution of hydrochloric acid and the benzene phase washed with a diluted aqueous solution of hydrochloric acid, with water until pH is bordering 7, then with an aqueous
45 solution of sodium bicarbonate until pH=8.5 and finally with water, the various aqueous washing agents being reextracted with benzene as they are obtained. The benzene phases are combined, dried on magnesium sulphate, 50 0.8 g of hydroquinone added, then some active charcoal, and the mixture agitated. The active charcoal and the sulphate were removed by filtration, 500 g of alumina added,

the mixture agitated, the alumina removed by filtration and the mixture concentrated to dryness by distillation, first under normal pressure, then under reduced pressure to obtain 940 g of d-allethrolone d-*trans*-chrysanthemate.

WHAT WE CLAIM IS:—

- 60 1. Insecticidal fumigating compositions of the type referred to comprising, as active ingredient, d-allethrolone d-*trans*-chrysanthemate together with a suitable carrier as herein defined.
2. Compositions as claimed in claim 1 containing 0.05 to 95% by weight of the active ingredient.
3. Compositions as claimed in claim 1 or claim 2 in a form whereby release of the active ingredient is effected by heating.
4. Compositions as claimed in any of the preceding claims wherein the said carrier comprises a combustible material.
5. Compositions as claimed in claim 4 wherein the combustible material comprises at least one of the following:— pyrethrum residue, Tabu powder, pyrethrum stalk powder, cedar leaf powder, wood powder, starch or coconut shell powder.
6. Compositions as claimed in claim 4 or claim 5 in the form of spirals or coils.
7. Compositions as claimed in any of claims 4 to 5 containing 0.05 to 10% by weight of the active ingredient.
8. Compositions as claimed in any of claims 1 to 3 wherein the said carrier comprises an incombustible fibrous substrate.
9. Compositions as claimed in any of claims 1 to 3 wherein the said carrier comprises an atomisable oil.
10. Compositions as claimed in any of the preceding claims further containing a stabiliser and/or a synergistic agent.
11. Compositions as claimed in claim 10 wherein the stabiliser comprises a phenol or arylamine.
12. Compositions as claimed in claim 10 or claim 11 wherein the synergistic agent comprises N-(2-ethylhexyl)-bicyclo-(2,2,1)-hepta-5-ene anhydrophthalic acid 2,3-dicarboximide or α -[2-(2-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyl-toluene.
13. Compositions as claimed in claim 1 substantially as herein described.
14. Insecticidal fumigating compositions as claimed in claim 1 substantially as herein described with reference to any of the Examples.
15. A method which comprises treating a fumigating composition as claimed in any of the preceding claims to effect release of an insecticidally effective amount of the active ingredient in or on a site containing, or liable to contain insects.
16. A method as claimed in claim 15 wherein the insects are mosquitos.



17. A method as claimed in claim 15 or claim 16 wherein the fumigating composition is heated or ignited to effect vaporisation of the active ingredient.
- 5 18. A method as claimed in claim 17 wherein heating or ignition of the fumigating composition is effected in a lamp.
19. A method as claimed in claim 15 substantially as herein described.
20. An insecticidal method as claimed in claim 15 substantially as herein described with reference to any of the Examples. 10

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