

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) INSECTICIDAL COMPOSITIONS

(71) We, SUMITOMO CHEMICAL COMPANY, LIMITED, a corporation organised under the laws of Japan, of 15, Kitahama-5-chome, Higashi-ku, Osaka, Japan, 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:—

This invention relates to a novel insecticidal composition in the form of a fumigant which contains as an active ingredient dl-2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl d-trans-chrysanthemate.

In the present specification, the effect of delaying the recovery of injurious insects knocked down is hereinafter referred to as the persistent effect, and the term "fumigant" means compositions which produce a vapour of an active ingredient by heating.

Oil sprays, aerosols, emulsifiable concentrates and dusts of pyrethrin and allethrin have widely been used in the past for sanitary purposes in particular environments because of their low toxicity to mammals and rapid knock down effect.

Investigations have been made in order to obtain an insecticide having more effective insecticidal activity with low toxicity to mammals than that of the conventional insecticides, and it has been found that an ester consisting of dl-allethrolone and d-trans-chrysanthemic acid (hereinafter referred to as the present ester) can display a specifically high insecticidal activity when used as a fumigant; the conditions of application are then entirely different from those used when applying oil sprays and aerosols, etc. This cannot easily be inferred theoretically, or from a knowledge of the insecticidal activity of said ester when applied in the form of an oil spray or the like.

It has been found that when the present ester is used in the form of a mosquito coil, which is of necessity subjected to heating, the present ester has several times the knock-down effect of the conventional allethrin product, i.e. so called technical grade allethrin which is an ester consisting of dl-allethrolone and dl-cis, trans-chrysanthemic acid, and it has been found that even when used in a form often used in practice, for example, as a dilute fumigant, the ester can maintain its insecticidal activity for a longer period of time than could be anticipated from the properties of a conventional mosquito coil of this kind.

Thus, according to the present invention there is provided an insecticidal composition in the form of a fumigant, as hereinbefore defined, containing as an active ingredient an effective amount of dl-2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl d-trans-chrysanthemate, and an inert carrier. The effective amount is within a range of 0.05 to 90% by weight.

The fumigant is usually a composition which produces a vapour on heating, which vapour can be used to kill or knock down insects by exposing them to it. This vapour can be exposed to insects in certain environments and thus free the environment from them.

Various examinations have been made concerning the relation between the allethrin isomers and their insecticidal activity, and it is well known that commercially available allethrins are mixtures of 8 isomers and, among these, an ester comprising d-allethrolone and d-trans-chrysanthemic acid displays the highest insecticidal activity and has 3.86 times the insecticidal activity of the allethrin product, when used in the

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form of an oil spray [W. A. Gersdorff and Narman Mitlin: J. Econ. Entmol., 46, page 999 (1953)].

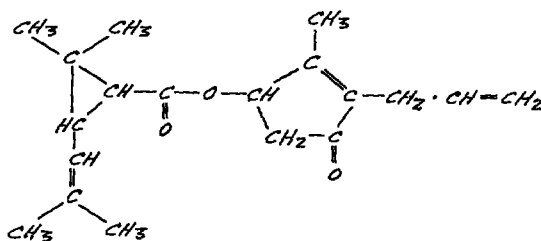
The industrial preparation of d-allethrolone, has however, not been successfully achieved, and it is also well known that in order to obtain an allethrin which is higher in insecticidal activity than that of the allethrin product available at present, an ester consisting of dl-allethrolone and d-trans-chrysanthemic acid may be prepared. For example, Ryo Yamamoto: "Noyakugaku (Agricultural Chemicals)" (published by Nanko-do on Mar. 15, 1963) discloses on page 73 the fact that the insecticidal activity on houseflies of the present ester is about 2 times the activity of the ester consisting of dl-allethrolone and dl-cis, trans-chrysanthemic acid, and recommends the use of the ester of d-trans-chrysanthemic acid in order to enhance the insecticidal activity of the allethrin product.

The insecticidal activities of the individual chemicals on adult houseflies and those of oil sprays thereof on adult houseflies and adult Northern house mosquitoes have been tested, and it was found that the insecticidal activity of the present ester is about 2.1 to 2.4 times the activity of allethrin. This was in agreement with the results given by Ryo Yamamoto.

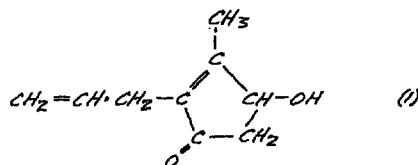
Until now, however, the ester formed using d-trans-chrysanthemic acid has not been put to practical use. This is ascribable to the fact that when used in the form of an oil spray, the ester of d-trans-chrysanthemic acid, which has no more than about 2 times the insecticidal activity of the ordinary allethrin product, is too low in insecticidal activity, in comparison with its production cost, to be used practically as an alternative to the allethrin product which is at present commercially available.

The surprising finding is that when used in the form of a fumigant such as in a mosquito coil, the present ester can give an insecticide having more rapid knock down and more persistent effects, which effects are most important for the control of injurious insects. This could not have been anticipated from conventional studies on allethrin isomers. We have confirmed that when formulated into the fumigant, the present ester gives an insecticidal composition which can have a rapid knock down effect which is about 4.2 to 5.6 times the effect of the ordinary allethrin product and can have a prominent persistent effect for a long period of time. The present insecticidal composition can be obtained more cheaply and have more excellent effects than the conventional allethrin product.

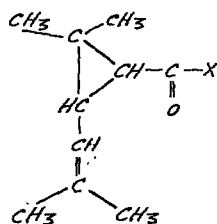
The present ester, dl - 2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl d - trans - chrysanthemate (N_D^{20} 1.5029) having the formula,



can be obtained easily and in high yield by reacting, in the presence of a hydrogen halide acceptor such as pyridine, dl-allethrolone represented by the formula (I),



with a d-trans-chrysanthemic acid halide represented by the general formula (II),



(II)

wherein X is a halogen atom.

Insecticidal compositions which contain the present ester as an active ingredient can be used as domestic insecticides for the control of sanitary injurious insects such as houseflies, mosquitoes, etc. and other injurious insects in houses, and are widely used in greenhouses, vinylhouses and storehouses to control insects injurious to stored cereals and to control insects injurious to agricultural and horticultural plant.

In the accompanying drawings, Fig. 1 shows the relation between concentration of active ingredients and KT_{50} (i.e. the time taken to knock down 50% of the insects) and thus illustrates the knock-down effect of oil sprays on adult Northern house mosquitoes; Fig. 2 shows the relation between concentration and KT_{50} and thus illustrates the knock-down effects of oil sprays on adult houseflies; Fig. 3 shows the relation between concentration and KT_{50} and illustrates the knock-down effects of mosquito coils on adult Northern house mosquitoes; Fig. 4 shows the relation between concentration and KT_{50} and illustrates the knock-down effects of mosquito coils on adult houseflies; and Fig. 5 shows the relation between time and knock-down ratio and illustrates the knock-down effects of the mosquito coils on adult Northern house mosquitoes.

In order to show that the properties of an insecticidal composition within the present invention could not have been anticipated from conventional examinations on the insecticidal activity of allethrin isomers, experimental examples and the results obtained are given below.

In the abovementioned drawings, and in the following Examples, percentages are by weight.

Experimental Example 1

Allethrin (an ester consisting of dl-allethrolone and dl-cis, trans-chrysanthemic acid) and the present ester were each diluted with acetone to a test concentration, and their insecticidal effects tested by a process in which the acetone solution was applied at the dorsum of the prothorax of the adult fly using a special microsyringe. The results of applying 50% lethal doses (LD_{50}) of the individual test solutions were as shown in Table I.

TABLE I

Test compound	LD_{50} (γ /fly)	Relative effect (at LD_{50})
Allethrin	0.85	1.0
Present ester	0.355	2.4

Experimental Example 2

Allethrin (the same compound as that used in Experimental Example 1) and the present ester were each dissolved in deodorized kerosene to a given concentration, and 0.7 ml. of each of the resulting solutions was sprayed by means of an atomizer into (70 cm)³ glass chambers. Twenty adult Northern house mosquitoes which had been allowed to live for 2 to 3 days after emergence or twenty houseflies which had been

allowed to live for 3 to 5 days after emergence had previously been introduced into each chamber. After the spraying, the number of knocked-down insects was observed at specific intervals of time. The 50% knock-down times (KT_{50}) obtained were as shown in Tables 2 and 3.

TABLE 2

Effects on adult Northern house mosquitoes

Test Compound	Concentration (%)	KT_{50} (sec.)	Relative effect in terms of comparison* of concentration			
			Concentration corresponding to 0.1% allethrin		Concentration corresponding to 0.2% allethrin	
			Concentration (%)	Relative effect	Concentration (%)	Relative effect
Allethrin	0.05	325	0.1	1.0	0.2	1.0
	0.1	225				
	0.2	138				
Present ester	0.05	210	0.041	2.4	0.096	2.1
	0.1	125				
	0.2	62				

*Refer to Fig. 1

TABLE 3

Effects on adult houseflies

Test Compound	Concentration (%)	KT ₅₀ (sec.)	Relative effect in terms of comparison** of concentration			
			Concentration corresponding to 0.1% allethrin		Concentration corresponding to 0.2% allethrin	
			Concentration (%)	Relative effect	Concentration (%)	Relative effect
Allethrin	0.05	360				
	0.1	282	0.1	1.0	0.2	1.0
	0.2	140				
Present ester	0.05	255				
	0.1	130	0.042	2.4	0.097	2.1
	0.2	72				

**Refer to Fig .2

The results shown in the above Experimental Examples 1 and 2 are in close agreement with the results from examination of conventional allethrin isomers, and show that the ratio of the insecticidal effect of the present ester, either in acetone solution or in the form of an oil spray, to allethrin is not more than about 2.1 to 2.4.

The effects of the present ester, when used as a fumigant, produced by heating are shown below with reference to Experimental Examples 3 and 4.

Experimental Example 3

Mosquito coils each containing 0.3%, 0.6% and 0.9% of allethrin (the same compound as that used in Experimental Example 1) and coils each containing 0.15%, 0.3% and 0.6% of the present ester were prepared.

A group of 20 adult Northern house mosquitoes or 20 adult houseflies was introduced into (70 cm)³ glass chambers. In order to test the effect of the coils on the Nor-

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thern house mosquitoes, 1 g. of each of the mosquito coils, and on the houseflies, 2 g. of each of the mosquito coils, were each ignited at both ends and placed at the centre of such a chamber. The number of knocked down insects was then counted to calculate the 50% knock-down times (KT₅₀). The results obtained were as shown in Tables 4 and 5.

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TABLE 4
Effects on Adult Northern house mosquitoes

Test Compound	Concentration (%)	KT ₅₀ (min. sec.)	Relative effect in terms of comparison of concentration*					
			Concentration corresponding to 0.3% allethrin		Concentration corresponding to 0.6% allethrin		Concentration corresponding to 0.09% allethrin	
			Concentration (%)	Relative effect	Concentration (%)	Relative effect	Concentration (%)	Relative effect
Allethrin	0.3	9' 42"	0.3	1.0	0.6	1.0	0.9	1.0
	0.6	8' 06"						
	0.9	7' 12"						
Present ester	0.15	7' 54"	0.067	4.5	0.132	4.5	0.192	4.7
	0.3	6'						
	0.6	4' 30"						

*Refer to Fig. 3

TABLE 5

Affects on adult houseflies

Test compound	Concentration (%)	KT ₅₀ (min. sec.)	Relative effect in terms of comparison of concentration**					
			Concentration corresponding to 0.3% allethrin		Concentration corresponding to 0.6% allethrin		Concentration corresponding to 0.9% allethrin	
			Concentration (%)	Relative effect	Concentration (%)	Relative effect	Concentration (%)	Relative effect
Allethrin	0.3	27'	0.3	1.0	0.6	1.0	0.9	1.0
	0.6	23'						
	0.9	18' 30"						
Present ester	0.15	21' 42"	0.054	5.6	0.137	4.4	0.215	4.2
	0.3	16' 36"						
	0.6	13' 0.6"						

**Refer to Fig. 4

Experimental Example 4

Mosquito coils, each containing 0.3% of allethrin (the same compound as that used in Experimental Example 1) and 0.3% of the present ester were prepared.

Into (70 cm)³ glass chambers were introduced 20 adult Northern house mosquitoes, and a battery-driven small electric fan having a blade diameter of 13 cm. was rotated in the chambers. Each of the mosquito coils of about 3 cm. in length was ignited at one end, burned for 2 minutes in such a glass chamber and then removed. After ignition of the mosquito coil, the number of knocked-down insects after certain intervals of time was counted for 120 minutes to calculate the knock-down ratio of the insects. The results obtained were as shown in Table 6.

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TABLE 6

Test compound	Combustion amount (mg./min.)	Knock-down ratio after certain times (%)										
		2'08"	3'	4'15"	6'	8'30"	12'	17'	24'	28'	34'	40'
Allethrin	90	6.9	12.7	27.5	40.2	61.8	73.5	80.4	88.2	92.2	90.2	90.2
Present ester	84	27.6	40.1	56.1	70.4	82.7	95.9	95.9	96.9	96.9	99.0	96.9

Test compound		Knock-down ratio after certain times (%)										
		48'	54'	60'	68'	74'	84'	94'	105'	120'	KT ₅₀ *	
Allethrin	82.4	84.3	78.4	72.5	66.7	68.6	63.7	63.7	63.7	61.8	7'06"	
Present ester	98.0	96.9	98.0	98.0	96.9	99.0	98.0	98.0	98.0	96.9	3'42"	

*Refer to Fig .5

As can be seen from the above Experimental Example 5, the present ester is shorter in 50% knock-down time (KT₅₀), and thus has a more rapid knock-down effect than allethrin. Further, allethrin shows a knock-down effect of more than 80% for about 40 minutes from 17 to 60 minutes after ignition, whereas the present ester can maintain a knock-down effect of more than 95% during a period from 8 to 120 minutes after ignition, i.e. over a period of time which is longer by more than about 110 minutes.

The present ester can be made up using a conventional procedure into a markedly effective mosquito coil by incorporating 0.05 to 5% by weight of the present ester as an active ingredient into a mosquito coil carrier, such as Tabu powder, marc, wood powder, starch and coconuts shell powder. Alternatively, the present ester is incorporated in an amount of 0.05 to 90% by weight into a fiber or like substrate, and the resulting fumigant is then placed on a hot plate heated, for example, electrically to a temperature of 120° to 400°C., when the active ingredient diffuses over a period of time and has a fumigant effect for a long period of time. As a further alternative, the present ester is made up into an oil spray of 0.05 to 90% by weight in concentration, and the oil spray is allowed to ascend by capillary action through a lamp-wick or the

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like and then heated, when a fumigant effect can also be obtained.

5 The present ester, which is an active ingredient of compositions within the present invention, may not only be used alone but may be incorporated with, as stabilizers, suitable amounts of phenol or bisphenol derivatives such as BHT, arylamines such as phenyl- α -naphthylamine, phenyl- β -naphthylamine or a condensation product of phenetidine with acetone, when compositions which have been more stabilized insecticidal effects can be obtained. Further, the compositions may be increased in insecticidal activity by the incorporation of synergists for pyrethroid type insecticides such as α - [2 - (2 - butoxyethoxy)ethoxy] - 4,5 - methylenedioxy - 2 - propyltoluene (hereinafter referred to as "piperonyl butoxide"), and N - (2 - ethylhexyl) - bicyclo(2,2,1)-hepta - 5 - ene - anhydrophthalic acid - 2,3 - dicarboximide (hereinafter referred to as "MGK-264"). 10

15 Procedures for the preparation of compositions within the present invention and their effects are illustrated below with reference to examples and test examples, but the scope of the present invention is not limited to the examples. 15

Example 1

20 A solution of 0.3 g. of the present ester in 5 ml. of methanol is thoroughly mixed with a mixture comprising 60 g. of pyrethrum marc, 30 g. of Tabu powder and 9.7 g. of wood powder. The resulting mixture is kneaded with about 100 ml. of water, and then shaped and dried to prepare 100 g. of a mosquito coil. 20

The product may optionally be coloured by the addition of 0.5% of Malachite Green or like dye, or may be incorporated with phenol or para-hydroxy-benzoate.

Example 2

25 A solution of 0.2 g. of the present ester in chloroform is uniformly adsorbed onto the surface of a piece of asbestos 2.5 cm. $\times$ 1.5 cm. in area and 0.3 cm. in thickness. Another asbestos piece of the same size is adhered to the asbestos piece so treated to obtain an insecticidal fumigant composition for use on an electrically heated plate. 25

Instead of asbestos, a pulp plate or like material equal in effect to asbestos may be used as the fibrous support.

Example 3

30 A solution of 0.2 g. of the present ester and 0.6 g. of MGK-264 in 5 ml. methanol is added to a mixture comprising 60 g. of pyrethrum marc, 30 g. of Tabu powder 9.2 g. of wood powder, and the resulting mixture is treated in the same manner as that described in Example 1 to obtain a mosquito coil. 30

35 Insecticidal effects of the present compositions obtained in the above manner as shown below with reference to test examples. 35

Test Example 1

40 In to a (70 cm)³ glass chamber were introduced about 50 adult Northern house mosquitoes, and 0.2 g. of one of the mosquito coils obtained by the methods described in Examples 1 and 3 was ignited at both ends and placed at the centre of the bottom of the chamber. Subsequently, the smoke inside the chamber was stirred by means of a small electric fan having a blade diameter of 13 cm., when each of the mosquito coils was found to knock down, within 15 minutes, more than 90% of the mosquito adults. 40

Test Example 2

45 Into a (70 cm)³ glass chamber were introduced about 50 adult houseflies. The insecticidal fumigant composition obtained by the method described in Example 2 was placed on an electric heater and placed at the centre of the bottom of the chamber, and an electric current was applied to the electric heater. Subsequently, the interior of the chamber was stirred by means of a small electric fan having a blade diameter of 13 cm., when more than 90% of the housefly adults were found to be knocked down within 20 minutes. 50

WHAT WE CLAIM IS:—

55 1. An insecticidal composition in the form of a fumigant, as hereinbefore defined, containing as an active ingredient an effective amount of dl-2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl d-trans-chrysanthemate, and an inert carrier. 55

2. An insecticidal composition according to Claim 1, wherein the effective amount is 0.05 to 90% by weight.

like and then heated, when a fumigant effect can also be obtained.

The present ester, which is an active ingredient of compositions within the present invention, may not only be used alone but may be incorporated with, as stabilizers, suitable amounts of phenol or bisphenol derivatives such as BHT, arylamines such as phenyl- α -naphthylamine, phenyl- β -naphthylamine or a condensation product of phenetidine with acetone, when compositions which have been more stabilized insecticidal effects can be obtained. Further, the compositions may be increased in insecticidal activity by the incorporation of synergists for pyrethroid type insecticides such as α - [2 - (2 - butoxyethoxy)ethoxy] - 4,5 - methylenedioxy - 2 - propyltoluene (hereinafter referred to as "piperonyl butoxide"), and N - (2 - ethylhexyl) - bicyclo(2,2,1)-hepta - 5 - ene - anhydrophthalic acid - 2,3 - dicarboximide (hereinafter referred to as "MGK-264").

Procedures for the preparation of compositions within the present invention and their effects are illustrated below with reference to examples and test examples, but the scope of the present invention is not limited to the examples.

Example 1

A solution of 0.3 g. of the present ester in 5 ml. of methanol is thoroughly mixed with a mixture comprising 60 g. of pyrethrum marc, 30 g. of Tabu powder and 9.7 g. of wood powder. The resulting mixture is kneaded with about 100 ml. of water, and then shaped and dried to prepare 100 g. of a mosquito coil.

The product may optionally be coloured by the addition of 0.5% of Malachite Green or like dye, or may be incorporated with phenol or para-hydroxy-benzoate.

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A solution of 0.2 g. of the present ester in chloroform is uniformly adsorbed onto the surface of a piece of asbestos 2.5 cm. $\times$ 1.5 cm. in area and 0.3 cm. in thickness. Another asbestos piece of the same size is adhered to the asbestos piece so treated to obtain an insecticidal fumigant composition for use on an electrically heated plate.

Instead of asbestos, a pulp plate or like material equal in effect to asbestos may be used as the fibrous support.

Example 3

A solution of 0.2 g. of the present ester and 0.6 g. of MGK-264 in 5 ml. methanol is added to a mixture comprising 60 g. of pyrethrum marc, 30 g. of Tabu powder 9.2 g. of wood powder, and the resulting mixture is treated in the same manner as that described in Example 1 to obtain a mosquito coil.

Insecticidal effects of the present compositions obtained in the above manner as shown below with reference to test examples.

Test Example 1

In to a (70 cm)³ glass chamber were introduced about 50 adult Northern house mosquitoes, and 0.2 g. of one of the mosquito coils obtained by the methods described in Examples 1 and 3 was ignited at both ends and placed at the centre of the bottom of the chamber. Subsequently, the smoke inside the chamber was stirred by means of a small electric fan having a blade diameter of 13 cm., when each of the mosquito coils was found to knock down, within 15 minutes, more than 90% of the mosquito adults.

Test Example 2

Into a (70 cm)³ glass chamber were introduced about 50 adult houseflies. The insecticidal fumigant composition obtained by the method described in Example 2 was placed on an electric heater and placed at the centre of the bottom of the chamber, and an electric current was applied to the electric heater. Subsequently, the interior of the chamber was stirred by means of a small electric fan having a blade diameter of 13 cm., when more than 90% of the housefly adults were found to be knocked down within 20 minutes.

WHAT WE CLAIM IS:—

1. An insecticidal composition in the form of a fumigant, as hereinbefore defined, containing as an active ingredient an effective amount of dl-2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl d-trans-chrysanthemate, and an inert carrier.

2. An insecticidal composition according to Claim 1, wherein the effective amount is 0.05 to 90% by weight.



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3. An insecticidal composition according to Claim 1 or Claim 2, wherein the composition is made up into a mosquito coil.

4. A method for killing insects, which comprises exposing insects to a vapour produced by heating an insecticidal composition of Claim 1.

5 5. A method for freeing a particular environment from living insects, which comprises exposing insects to a vapour produced by heating an insecticidal composition of Claim 1. 5

6. Insecticidal compositions according to Claim 1 substantially as herein described and exemplified.

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