

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 an insecticidal composition in the form of a fumigant containing, as an active ingredient, a mixture prepared by mixing in suitable proportions dl - 2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl dl - cis, trans - chrysanthemate (hereinafter referred to as "allethrin") and 5 - benzyl - 3 - furylmethyl - dl - cis, trans - chrysanthemate (hereinafter referred to as "Chrysron" which is a registered trade mark of an insecticide produced by Sumitomo Chemical Co Ltd), or 5 - benzyl - 3 - furylmethyl - d - trans - chrysanthemate (hereinafter referred to as "d-trans-Chrysron"), which is an optical isomer of Chrysron.

The term "fumigant" means in this specification a composition which, when used as an insecticide, is subjected to heating to obtain the desired insecticidal effect.

Recently, the control of insects harmful to health such as mosquitoes, which are carriers of cerebritis, filaria and other infectious diseases, has become a serious problem. It is of importance in the control of such injurious insects to be able to quickly knock them down and kill them to prevent them from sucking the blood of mammals. For controlling such insects, mosquito coils, which in most cases contain either allethrin or pyrethrin as an active ingredient have previously been used. These insecticides, however, do not always have sufficient killing effect, although they can have rapid knock down effect.

It has also been found that either Chrysron or d-trans-Chrysron when used alone has an excellent killing effect when used in the form of an oil spray or aerosol, but has so inferior a knock down effect, compared to that of allethrin and pyrethrin, that it is not, in practice,

useful alone, particularly when in the form of mosquito coils.

As a result of extensive studies aimed at providing insecticides having higher insecticidal activities with low toxicity to mammals, it has now been found that when allethrin and Chrysron or allethrin and d-trans-Chrysron are incorporated into a mixture, they display synergistic effects not only in their knock down effect but also in their killing effect on various injurious insects.

When the mixture is used in conventional forms such as in oil sprays, aerosols or emulsifiable concentrates, however, marked advantages cannot always be obtained in practice, even if the insecticidal activities of the effective compounds contained therein are synergistically increased, and, in fact, other excellent insecticides are known which contain a mixture of Chrysron and phthalthrins (N - (chrysanthemoxymethyl) - 3,4,5,6 - tetrahydro - phthalimide), and which have been found to have far more marked insecticidal activities when used in the forms particularly mentioned above than a composition containing a mixture of allethrin and Chrysron or d-trans-Chrysron.

As a result of further extensive studies it has further been found that, if when using compositions containing a mixture of allethrin and Chrysron, or allethrin and d-trans-Chrysron, as insecticides, they are subjected to heating (the conditions of application are thus, in these cases, different from those when the compositions are applied in the form of, for example, oil sprays or aerosols), strong synergistic effects of these compounds can be exhibited and thus these compositions display a surprisingly higher insecticidal effect than could be predicted from the effects displayed when the composition is used in the form of, for example, an oil spray.

Thus, surprisingly it has been found that the compounds in a mixture of allethrin and Chrysron or a mixture of allethrin and d-trans-Chrysron in the form of a fumigant show synergism in the knock down effect exhibited on heating and further that they can substantially delay the recovery of insects knocked down. In

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the present specification the effect of delaying the recovery of insects knocked down is herein-after referred to as the persistent effect.

5 According to the present invention there is provided an insecticidal composition in the form of a fumigant containing, as an active ingredient, an effective amount of a mixture of allethrin and Chrysron or a mixture of allethrin and d-trans-chrysron, and an inert carrier, the weight ratio of allethrin to Chrysron or d-trans-Chrysron in the mixture preferably being in a range of from 10:0.5 to 10:30.

10 According to the present invention there is also provided a method for killing insects or

removing them from a particular environment which includes exposing them to the vapour produced by heating an insecticidal composition. Parts and percentages referred to herein-after are by weight.

The accompanying drawing shows the relation between time and knock down ratio obtained from tests illustrating the knock down effects of individual mosquito coils on adult Northern house mosquitoes.

25 In order to further clarify the excellent effects of compositions within the present invention, an experimental example and the results obtained are shown below.

TABLE

Sample No.	Composition	Amount of mosquito coil burned (mg/min)	Knock-down ratio with lapse of time							
			2'08"	3'	4'15"	6'	8'30"	12'	17'	
1	Allethrin 0.3%	45	0	2.0	5.1	9.2	19.4	30.6	51.0	
2	Chrysron 0.3%	47	0	0	0	0	0	3.1	6.1	
3	d-trans-chrysron 0.3%	47	0	0	0	3.0	6.0	12.0	17.0	
4	A mixture of Allethrin 2: Chrysron 1 0.3%	50	1.0	6.0	14.0	26.0	43.0	57.0	64.0	
5	A mixture of Allethrin 5: d-trans-Chrysron 1 0.3%	46	2.0	8.1	16.2	30.3	48.5	65.7	74.7	
6	A mixture of Allethrin 2: Chrysron 1 0.15%	50	1.0	5.0	10.0	17.0	31.0	35.0	47.0	
7	A mixture of Allethrin 5: d-trans-Chrysron 1 0.15%	48	3.1	9.2	13.3	21.4	32.7	38.8	54.1	

Experimental Example

5 Mosquito coils each containing 0.3% of allethrin, Chrysron and d-trans-Chrysron alone were prepared. Similarly, mosquito coils each containing 0.3% and 0.15% of a mixture of allethrin and Chrysron in a weight ratio of 2:1 and a mixture of allethrin and d-trans-Chrysron in a weight ratio of 5:1 were prepared.

10 A group of 20 adult Northern house mosquitoes were introduced into a (70 cm)³ glass chamber, and a battery driven small motor fan (13 cm in blade diameter) was placed in the chamber and rotated. Thereafter, each mos-

quito coil, cut to a length of about 3 cm, was ignited at one end, burned for 1 minute in the chamber and then removed. After ignition of the mosquito coil, the number of knocked-down mosquitoes was counted with lapse of time for 120 minutes to calculate the knock down ratio at each time. A 50% knock down time was also calculated (i.e. KT_{50}). Further, the theoretical KT_{50} value of each mixture was calculated using the equation of Yun-Pei Sun et al. [J. Econ. Entomology, 53, 887 (1960)], and compared with the actual KT_{50} value. The results obtained are shown in the Table given below and the accompanying drawing.

Knock down ratio with lapse of time														
24'	28'	34'	40'	48'	54'	60'	68'	75'	84'	94'	105'	120'	Found KT_{50}	Theoretical KT_{50}
66.3	71.4	80.6	80.6	75.5	69.4	67.3	62.2	49.0	44.9	42.9	40.8	31.6	17'	—
9.2	12.2	20.4	22.4	35.7	38.8	51.0	53.1	64.3	67.3	78.6	82.7	78.6	59'30"	—
26.0	29.0	38.0	46.0	54.0	64.0	70.0	76.0	84.0	88.0	92.0	90.0	92.0	44'	—
78.0	83.0	89.0	89.0	92.0	92.0	91.0	93.0	93.0	94.0	94.0	93.0	94.0	10'12"	22'15"
87.9	93.9	96.0	96.0	97.0	97.0	96.0	98.0	98.0	99.0	99.0	98.0	99.0	8'54"	18'58"
59.0	71.0	79.0	79.0	81.0	83.0	83.0	82.0	82.0	85.0	85.0	82.0	84.0	18'48"	—
64.3	77.6	82.7	83.7	82.7	85.7	86.7	86.7	88.8	89.8	87.8	88.8	88.8	15'30"	—

It can be seen from the Table that the KT_{50} values found for Sample Nos. 4 and 5 are below the theoretical KT_{50} values, thus showing that the effective compounds incorporated into the mixture represented by these Sample Nos. exhibit excellent synergism in their knock-down effect. Similarly, it can also be seen that the knock-down effects measured for Sample Nos. 6 and 7 are comparable with that for Sample No. 1, thus showing that these mixtures have a knock-down effect nearly twice as great as that of a composition containing allethrin alone. Moreover, it is clear that the effective compounds incorporated in these mixtures exhibit surprisingly excellent synergism in their knock-down effect after a long period of time (i.e. their persistent effect), the effect being more than 16 times that of the composition containing allethrin alone at 80% knock down ratio.

Compositions within the present invention in the form of fumigants can be extensively employed as insecticides for domestic use for the control of so-called sanitary injurious insects such as flies and mosquitoes, for use in green houses, vinyl houses and warehouses, and for agricultural and horticultural purposes to control insects injurious to, for example, stored cereals.

Such a composition can be made up using any conventional procedure into a markedly effective mosquito coil by incorporating 0.05 to 5% by weight of the mixture of the active ingredients into a mosquito coil carrier, such as Tabu powder, marc, wood powder, starch or coconut shell powder. Alternatively, 0.05 to 90% by weight of the mixture can be incorporated into a fibre or like substrate, which substrate can then be placed on an electrically heated hot plate and heated to a temperature of 120° to 400°C, when the active ingredient diffuses over an interval of time to give the desired insecticidal effect for a long period of time. A composition within the present invention can also be made up into an oil spray of 0.05 to 90% by weight concentration, which oil spray is then caused to rise by capillary action through, for example, a lamp-wick, and then heated, when the desired insecticidal effect can be observed.

The mixture which is an active ingredient of compositions within the present invention, may be used alone or may be incorporated with, suitable amounts of, for example, stabilizers, such as phenol or bisphenol derivatives, e.g. butylhydroxytoluene, or arylamines, e.g. phenyl- α -naphthylamine, phenyl- β -naphthylamine or the condensation product of phenetidine with acetone, when compositions having more stabilized insecticidal effects can be obtained. Further, the compositions may be increased in their insecticidal activity by the incorporation of synergists for pyrethroid type insecticides such as α -[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyl-

toluene (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 with the present invention and effects thereof are illustrated below with reference to examples and test examples, but these do not limit the scope of the present invention.

Example 1

Four portions, each of 0.05 grams of Chrysron are mixed with 0.3 g, 0.25 g, 0.2 g and 0.15 g of allethrin, respectively, and each mixture is dissolved in 5 ml of methanol. This solution is mixed with a mosquito coil carrier (a 3:5:1 mixture of Tabu powder, pyrethrum marc and wood flour) to make the total amount up to 100 g, and the resulting mixture is uniformly stirred. After evaporating the methanol, the mixture is kneaded with 150 ml of water, and then shaped and dried to obtain a mosquito coil.

If necessary, the mosquito coil may be coloured by the addition of 0.5% of a dye such as Malachite Green, or may be incorporated with a phenol or p-hydroxybenzoic acid ester.

Example 2

Three portions, each of a mixture comprising 0.15 g of Chrysron and 0.1 g of butylated hydroxytoluene (2,6-di-tert-butyl-p-cresol) are mixed with 0.2 g, 0.15 g, 0.1 g and 0.05 g of allethrin respectively, and each resulting mixture is dissolved in 5 ml of methanol. This solution is treated in the same manner as that described in Example 1 to obtain the respective mosquito coils.

Example 3

Four portions, each of 0.025 grams of d-trans-Chrysron are mixed with 0.325 g, 0.275 g, 0.225 g, 0.175 g and 0.125 g of allethrin, respectively, and such resulting mixture is dissolved in 5 ml of methanol. This solution is treated in the same manner as that described in Example 1 to obtain the respective mosquito coils.

Example 4

Five portions each of a mixture comprising 0.1 g of d-trans-Chrysron and 0.6 g of MGK-264 are mixed with 0.25 g, 0.2 g, 0.15 g, 0.1 g and 0.05 g of allethrin respectively, and each resulting mixture is dissolved in 5 ml of methanol. This solution is treated in the same manner as that described in Example 1 to obtain respective mosquito coils.

Example 5

A mixture comprising 0.2 g of allethrin and 0.1 g of Chrysron and a mixture comprising 0.2 g of allethrin and 0.05 g of d-trans-Chrysron are each dissolved in methanol. These solutions are each uniformly adsorbed on the surface of an asbestos piece of 2.5 cm $\times$ 1.5 cm in area and 0.3 cm in thickness. Onto the asbestos surface is pasted another asbestos piece of identical size to obtain respective in-

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secticidal fibrous fumigant compositions for use on an electrically heated plate. Alternatively to asbestos, a pulp sheet of like material which is identical in effectiveness may be used as the fibrous carrier.

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

Test Example 1

Into a (70 cm)³ glass chamber were introduced about 50 adult Northern house mosquitoes. 0.2 Grams of each of the mosquito coils obtained by the methods described in Examples 1, 2, 3 and 4 was ignited at both ends placed centrally at the base of the chamber. The smoke inside the chamber was circulated by means of a battery driven small motor fan (blade diameter 13 cm). As a result, it was found that every mosquito coil could knock down more than 90% of the adult mosquitoes within 20 minutes and could kill more than 80% of the insects by the next day.

Test Example 2

Into a (70 cm)³ glass chamber were introduced about 50 adult house flies. Each of the insecticidal fibrous fumigant compositions obtained by the method described in Example 5 was placed on electric heating means, which means was then placed centrally of the base of the chamber. Subsequently, an electric current was applied to the heating means, and the smoke in the interior of the chamber was circulated by means of a battery driven motor fan (blade diameter 13 cm). As a result, it was found that every composition could kill more than 80% of the adult house flies within 20 minutes, and could kill more than 80% of these insects by the next day.

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 a mixture of (1) dl - 2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl dl - cis, trans - chrysanthemate and (2) 5 - benzyl - 3 - furylmethyl dl - cis,trans - chrysanthemate or 5 - benzyl - 3 - furylmethyl - 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 based on the weight of the composition.

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

4. An insecticidal composition according to Claim 1, Claim 2 or Claim 3 wherein the weight ratio of dl - 2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl dl - cis, trans - chrysanthemate to 5 - benzyl - 3 - furylmethyl - dl - cis,trans - chrysanthemate or 5 - benzyl - 3 - furylmethyl - d - trans - chrysanthemate is from 10:0.5 to 10:30 inclusively.

5. A method for killing insects or for removing them from a particular environment, which includes exposing them to the vapour produced by heating an insecticidal composition according to Claim 1.

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

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secticidal fibrous fumigant compositions for use on an electrically heated plate. Alternatively to asbestos, a pulp sheet of like material which is identical in effectiveness may be used as the fibrous carrier.

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Test Example 2

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2. An insecticidal composition according to claim 1, wherein the effective amount is 0.05 to 90% by weight based on the weight of the composition.
3. An insecticidal composition according to Claim 1, or Claim 2 wherein the composition is formulated into a mosquito coil.
4. An insecticidal composition according to Claim 1, Claim 2 or Claim 3 wherein the weight ratio of dl - 2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl dl - cis, trans - chrysanthemate to 5 - benzyl - 3 - furylmethyl - dl - cis,trans - chrysanthemate or 5 - benzyl - 3 - furylmethyl - d - trans - chrysanthemate is from 10:0.5 to 10:30 inclusively.
5. A method for killing insects or for removing them from a particular environment, which includes exposing them to the vapour produced by heating an insecticidal composition according to Claim 1.
6. Insecticidal compositions according to Claim 1 substantially as herein described and exemplified.

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