

PATENT SPECIFICATION

(11) 1336 230

1336 230

DRAWINGS ATTACHED

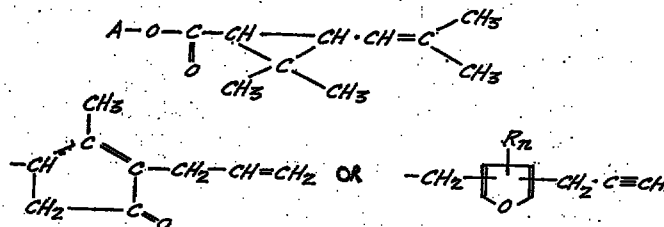
- (21) Application No. 36254/71 (22) Filed 2 Aug. 1971
 (31) Convention Application No. 68124 (32) Filed 3 Aug. 1970
 (31) Convention Application No. 72512 (32) Filed 19 Aug. 1970 in
 (33) Japan (JA)
 (44) Complete Specification published 7 Nov. 1973
 (51) International Classification A01N 9/24, 9/02, 9/08 // 17/02,
 17/0 X
 (52) Index at acceptance
 A5E 1A1J 1A2P 1A3F 1A5B2 1C14 1C2K



(54) INSECTICIDAL COMPOSITIONS CONTAINING CHRYSANTHEMATES

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation organized 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 provides an insecticidal composition in the form of a fumigant, (i.e. a composition which is effective on heating, and hereinafter called a "fumigant") which comprises an inert carrier and as an essential ingredient a *d*-cis-isomer of a chrysanthemate, or a mixture of isomers of a chrysanthemate which mixture contains more than 15% by weight of the mixture of the *d*-cis-isomer and which chrysanthemate has the formula (I), wherein A is



in which R is a hydrogen atom or a methyl group, and *n* is 1 or 2.

A composition within the present invention can be employed as an inexpensive insecticidal fumigant which is low in toxicity and rapid in knock down effect, and hence can be used for sanitary purposes and for agricultural and horticultural purposes.

Thus the present invention also provides an insecticidal composition in the form of, for example, a mosquito coil, and a method of killing insects, or of freeing a particular environment therefrom, which comprises exposing the insects to the vapour produced by heating such an insecticidal composition.

In the past, oil sprays, aerosols and mosquito coils of pyrethrin and allethrin have widely been used as insecticides for environment sanitation because of their low toxicity to mammals and rapid knock down effect.

Recently, the control of insects harmful to mammals such as mosquitoes, which are vectors of cerebritis, filaria and similar infectious diseases, has come to be a serious problem. What is of importance in the control of these harmful insects is to quickly knock down the insects, to kill them, and to inhibit their blood-sucking actions on mammals.

During the course of studies carried out for the purpose of obtaining insecticides having a rapid knock down effect as well as a strong killing effect with low toxicity to mammals, it was found that the *d*-cis-isomer of a chrysanthemate represented by the formula (I) displayed far better insecticidal activities than the *d*-trans-isomer, particularly when used in the form of, for example, a mosquito coil which is, of necessity, subjected to heating. Surprisingly, results were obtained which were entirely different

from those expected from the established theory concerning the relation between isomers and their insecticidal effects when using conventional chrysanthemate type insecticides, i.e. the theory that in the case of, for example, allethrin, the *d*-trans-chrysanthemate displays the most excellent insecticidal effects. The discovery confirmed that *d*-cis-isomer can be put into practical use with economic advantage.

It is well known that among the chrysanthemate type insecticides, allethrin, the isomers of which have previously been most extensively studied, has 8 isomers, and it is also well known that the said isomers are different from one another in their insecticidal effect. For example, M. Elliott et al. disclosed, in J. Sci. Food Agr. 20, No. 9, 561—65 (1969), the fact that when the insecticidal effect of the *dl*-trans-chrysanthemate of allethrolon is taken as 100, the relative effect of *dl*-cis-chrysanthemate is 48, i.e. about 1/2 of the effect of said *dl*-trans-chrysanthemate, and when the insecticidal effect of the *d*-trans-chrysanthemate of allethrolon is taken as 100, the relative effect of *d*-cis-chrysanthemate is 25, i.e. about 1/4 of the effect of said *d*-trans-chrysanthemate. Thus, it has widely been known for the allethrin isomers, that the cis-isomer as an acid component is obviously inferior in insecticidal effect to the trans-isomer. Therefore, it has been considered that in order to increase the insecticidal effects of allethrin products, the use of *d*-trans-chrysanthemate is most desirable.

As mentioned previously, however, we have found, during the course of extensive studies on isomers of the chrysanthemates represented by the formula (I), that *d*-cis- and *dl*-cis-isomers of these chrysanthemates, when used in the form of fumigants such as in mosquito coils, which are, of necessity, subjected to heating, were found to display more excellent insecticidal effects than those of esters of *dl*-cis, trans-chrysanthemic acid (a technical grade product obtained by conventional processes) and the corresponding esters of *dl*-trans- or *d*-trans-chrysanthemic acids, and have obtained results which contradict the established theory concerning the relation between isomers and insecticidal effects of the conventional chrysanthemate type insecticides.

From the above-mentioned studies, we have found that in order to enhance the insecticidal effects of industrial products of the chrysanthemates represented by the aforesaid formula (I), it is best to use esters rich in *d*-cis-chrysanthemic acid.

The chrysanthemate represented by the formula (I) when prepared by conventional synthetic methods is a mixture comprising 70% of *dl*-trans-isomer and 30% of *dl*-cis-isomer, which latter contains 15% of a *d*-cis-isomer and 15% of an *l*-cis-isomer. If, however, the content of the *d*-cis-isomer in said ester is increased to more than 15% by enrichment of *d*-cis-isomer, (or of the abovementioned *dl*-cis-isomer), and preferably to more than 18%, then the higher the content of *d*-cis-isomer, and the greater the insecticidal effect. In other words, the chrysanthemates incorporated into compositions of the present invention contain, of necessity, more than 15% of the *d*-cis-isomer and contain less than 85% of any isomer other than *d*-cis-isomer.

While it is known at present that *d*-trans-chrysanthemates of allethrolon are superior in their insecticidal activities to the conventional technical allethrin products, the greatest drawback encountered in commercial scale production thereof lies in that when using a known process for producing chrysanthemic acid, trans- and cis-isomers are formed in a ratio of about 70:30, and in the past, no use for the by-product cis-chrysanthemic acids was found and hence these were separated, isomerized or discarded, with the result that the desired *d*-trans-chrysanthemates become expensive.

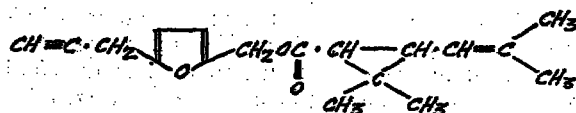
In view of the above, it is of commercial importance that more than 15% of *d*-cis-chrysanthemic acids (which may be isolated or may be employed in compositions in the form of or derived from a racemic *dl*-cis-isomer) according to the present invention are found to have prominent effects as insecticides and can be put into practical use, since these practically useful insecticides can be obtained with marked economic advantages by using as starting materials cis-chrysanthemic acids which are by-products of the production of the conventional trans-chrysanthemates, which themselves have excellent insecticidal activities.

Examples of useful compounds used in compositions within the present invention (hereinafter called "the present compounds") include the *d*-cis-chrysanthemates of the compounds (1) to (7) given below.

Compound
No.

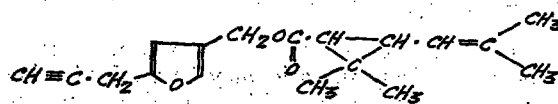
Structure

(1)



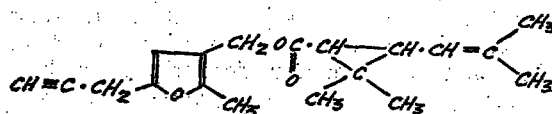
5-Propargyl-furfuryl chrysanthemate

(2)



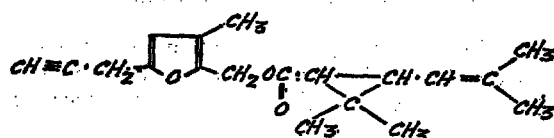
5-Propargyl-3-furylmethyl chrysanthemate

(3)



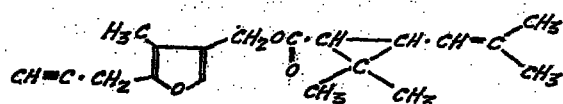
2-Methyl-5-propargyl-3-furylmethyl chrysanthemate

(4)



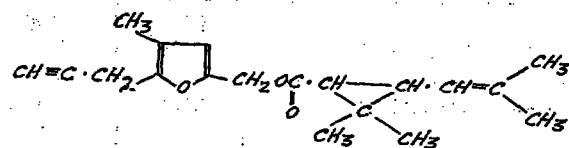
3-Methyl-5-propargyl-furfuryl chrysanthemate

(5)



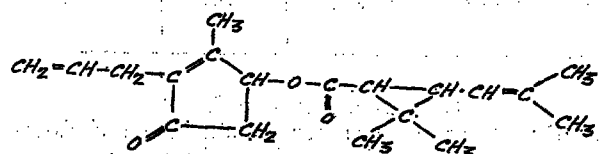
4-Methyl-5-propargyl-3-furylmethyl chrysanthemate

(6)



4-Methyl-5-propargyl-furfuryl chrysanthemate

(7)



2-Allyl-3-methyl-cyclopent-2-ene-4-yl chrysanthemate

The esters used according to the present invention can be obtained, for example, by reacting a corresponding furylmethyl alcohol or allethrolool with a *d*-cis-chrysanthemic acid or a reactive derivative thereof (i.e. a compound wherein the carbonyl group is replaced by a group which is itself capable of reaction with the alcohol), optionally in the presence of a suitable adjuvant. The reactive derivative referred to above includes acid halides, anhydrides, lower alkyl esters and alkali metal salts. The alcohol may also be used, in some cases, in the form of a reactive derivative such as the *p*-toluenesulfonate. Further, a *dl*-cis-isomer, i.e. a racemic isomer, which contains more than 15% of *d*-cis-isomer may also be used effectively.

Chrysanthemic acid synthesized by a conventional procedure, which contains a mixture of *dl*-cis, and *dl*-trans-isomers having a trans to cis ratio of about 70:30, easily gives a *dl*-cis-chrysanthemic acid when recrystallized from ethyl acetate, as reported by, for example, I. G. M. Campbell and S. H. Harper in Journal of Chemical Society, page 284 (1945). Alternatively, such a mixture is heated with stirring in benzene together with a boron trifluoride-ether complex to convert the *dl*-cis-chrysanthemic acid into *dl*-dihydrochrysanthemolactone, which is then separated from the *dl*-trans-chrysanthemic acid by extraction with an aqueous sodium hydroxide solution and thereafter ring-opened by acidification with sulfuric acid to obtain the *dl*-cis-chrysanthemic acid.

The *dl*-cis-chrysanthemic acid thus obtained may then be esterified to obtain a *dl*-cis-chrysanthemate, or alternatively the acid may be resolved using a suitable optical resolving agent, e.g. (+)- α -*p*-methylbenzyl-benzylamine, and the resulting *d*-cis-chrysanthemic acid may then be esterified to obtain a *d*-cis-chrysanthemate.

The insecticidal fumigant compositions of the present invention which each contain an ester as described above as active ingredient can be extensively used as insecticides not only for domestic use for the control of insects harmful to health such as houseflies, mosquitoes and similar harmful domestic insects, but also for use in glass or plastics greenhouses, or warehouses, and for agricultural and horticultural purposes to control insects harmful to stored cereals and to agriculture and horticulture.

The following examples are shown in order to clarify the fact that compositions within the present invention behave in a manner contradictory to established theory concerning the relation between isomers and insecticidal effects of conventional allethrins.

In the first place, the fact that compositions within the present invention, when applied as drops or when used in the form of oil sprays, display effects such as those expected, is shown below with reference to Experimental Examples 1 and 2 which we carried out.

Experimental Example 1.

Samples of allethronyl *d*-cis-chrysanthemate, allethronyl *d*-trans-chrysanthemate and a commercial allethrin product (containing 7.5% of *d*-cis-isomer) were each diluted with acetone to a test concentration, and the insecticidal effect of the resulting compositions was tested by dropping a trace amount of the compositions onto the dorsum of the prothorax of an adult housefly using a microsyringe. As a result, the LD₅₀ of the individual compositions after 24 hours shown in Table 1 were observed.

TABLE 1

Test compound	LD ₅₀ (γ /fly)	Relative effectiveness
Allethronyl <i>d</i> -cis-chrysanthemate	0.85	0.97
Allethronyl <i>d</i> -trans-chrysanthemate	0.27	3.00
Commercial allethrin product (containing 7.5% of <i>d</i> -cis-isomer)	0.82	1.00

Experimental Example 2.

A given amount of each of the Compounds allethronyl *d*-cis-chrysanthemate, allethronyl *d*-trans-chrysanthemate, allethronyl *dl*-cis-chrysanthemate, allethronyl *dl*-cis,trans-chrysanthemate (containing 15% of *d*-cis-isomer) and a commercial allethrin product (containing 7.5% of *d*-cis-isomer) was dissolved in deodorized kerosene, and 0.7 ml of the resulting solution was sprayed using an atomizer into a (70 cm)³ glass chamber, into which had been introduced a group of about 20 adult northern house mosquitoes. After the spraying, the number of knocked-down mosquitoes was counted at definite intervals for 10 minutes. After repeating the above operation several times, the KT₅₀ of the mosquitoes was calculated. Further, the mosquitoes knocked down within a period of 10 minutes were collected and allowed to stand in an observation cage, in which a bait had been placed, and the number of insects killed was counted to calculate the ratio of insects killed. The results obtained were as shown in Table 2 and Fig. 1.

TABLE 2

Oil spray		KT ₅₀ (sec.)	Relative effectiveness according to comparison* in concentration				Ratio of killed insects (%)
			Concentration corresponding to the effectiveness of 0.1% allethrin		Concentration corresponding to the effectiveness of 0.2% allethrin		
			Concen- tration (%)	Effectiveness ratio	Concen- tration (%)	Effectiveness ratio	
Test compound	Concen- tration (%)						
Allethronyl <i>d</i> -cis- chrysanthemate	0.05	442	0.2	0.5	0.34	0.6	50
	0.1	360					65
	0.2	220					86
Allethronyl <i>d</i> -trans- chrysanthemate	0.05	225	0.047	2.1	0.098	2.0	64
	0.1	134					89
	0.2	67					100
Allethronyl <i>dl</i> -cis- chrysanthemate	0.05	509	0.31	0.32	0.54	0.37	52
	0.1	408					80
	0.2	292					
Allethronyl <i>dl</i> -cis, trans- chrysanthemate (containing 15% of <i>d</i> -cis-isomer)	0.05	350	0.122	0.8	0.232	0.9	51
	0.1	256					65
	0.2	164					87
Commercial allethrin product (containing 7.5% of <i>d</i> -cis-isomer)	0.1	232	0.1	1.0	0.2	1.0	68
	0.2	145					87

* A value calculated by inserting the KT₅₀ value of each of 0.1% and 0.2% oil sprays of allethrin product into the concentration-KT₅₀ graph of Fig. 1.

The results shown in the above Experimental Examples 1 and 2 are in good agreement with the results of examinations of the conventional allethrin isomers, and indicate that allethronyl *d*-trans-chrysanthemate is superior in insecticidal effect to allethronyl *d*-cis-chrysanthemate under the particular conditions of application employed.

In the next place, the effects of fumigant compositions within the present invention are shown below with reference to Experimental Examples 3 and 4.

Experimental Example 3.

A series of nine mosquito coils each containing either 0.15%, 0.3% or 0.6% of either allethronyl *d*-cis-chrysanthemate, allethronyl *d*-trans-chrysanthemate, or allethronyl *dl*-cis-chrysanthemate were prepared.

For comparison, a series of mosquito coils each containing either 0.3%, 0.6% or 0.9% of an allethrin product, which is most frequently used at present, or a mixture of allethronyl *dl*-cis and trans-chrysanthemates (containing 15% of the *d*-cis-isomer).

Into a (70 cm)³ glass chamber was introduced a group of about 20 northern house mosquitoes, and 1g of each of the above-mentioned mosquito coils was ignited at both ends and placed at the centre of the bottom of the chamber. The number of knocked down mosquitoes was then counted with lapse of time for 24 minutes. After repeating the above operation several times, the 50% knock down time (KT₅₀) of the mosquitoes was calculated. Further, the mosquitoes knocked down within a period of 24 minutes were collected and allowed to stand overnight at room temperature in an observation cage, in which a bait had been placed, and the number of insects killed was counted to calculate the ratio of insects killed. The results obtained were as shown in Table 3 and Fig. 2.

TABLE 3

Mosquito coil		KT ₅₀ (min. sec.)	Relative effectiveness according to comparison* in concentration						Ratio of killed insects (%)
			Concentration corresponding to the effectiveness of 0.3% allethrin			Concentration corresponding to the effectiveness of 0.6% allethrin		Concentration corresponding to the effectiveness of 0.9% allethrin	
			Concen- tration (%)	Effectiveness ratio	Concen- tration (%)	Effectiveness ratio	Concen- tration (%)	Effectiveness ratio	
Test compound	Concen- tration (%)								
Allethronyl <i>d</i> -cis- chrysanthemate	0.15	6'42"							76
	0.3	4'42"	0.053	5.7	0.091	6.6	0.127	7.1	93
	0.6	2'54"							98
Allethronyl <i>d</i> -trans- chrysanthemate	0.15	7'48"							72
	0.3	6'12"	0.075	4.0	0.14	4.3	0.205	4.4	90
	0.6	4'24"							96
Allethronyl <i>dl</i> -cis- chrysanthemate	0.15	9'42"							60
	0.3	8'00"	0.168	1.8	0.295	2.0	0.410	2.2	74
	0.6	5'54"							91
Allethronyl <i>dl</i> -cis,trans- chrysanthemate (Containing 15% of <i>d</i> -cis-isomer)	0.3	9'18"							75
	0.6	7'36"	0.267	1.1	0.510	1.2	0.760	1.2	91
	0.9	6'42"							100
Allethrin product (containing 7.5% of <i>d</i> -cis-isomer)	0.3	9'30"							71
	0.6	8'00"	0.3	1.0	0.6	1.0	0.9	1.0	90
	0.9	7'06"							100

* A value calculated by inserting the KT₅₀ value of each of 0.3%, 0.6% and 0.9% mosquito coils of allethrin product into the concentration-KT₅₀ graph of Fig. 2

3

(B)

Experimental Example 4.

A series of mosquito coils each containing either 0.15%, 0.3% or 0.6% of a *d*-cis-, *l*-cis- or *d*-trans-isomer of the previously exemplified compound (1); a mixture comprising 70% of the *dl*-trans-isomer and 15% of the *dl*-cis-isomer; and a *dl*-cis-, *d*-cis-, *dl*-trans- or *d*-trans-isomer of the exemplified compound (3) were prepared.

For comparison, a mosquito coil containing 0.6% of commercial allethrin (containing 5% of *d*-cis-isomer), which is most frequently used at present was prepared.

Into a (70 cm)³ glass chamber was introduced a group of about 20 northern house mosquito, and 1 g of each of the abovementioned mosquito coils was ignited at both ends and placed at the centre of the bottom of the chamber. The number of knocked down mosquitoes was then counted with lapse of time for 24 minutes. After repeating the above operation several times, the 50% knock down time (KT₅₀) of the mosquitoes was calculated. Further, the mosquitoes knocked down within a period of 24 minutes were collected and allowed to stand overnight at room temperature in an observation cage, in which a bait had been placed, and the number of insects killed was counted to calculate the ratio of insects killed. The results obtained were as shown in Table 4 and Figs. 3 and 4, in which the compounds of the present invention are represented by the numbers of the previously exemplified compounds.

TABLE 4

Composition		K.T. ₅₀ (min. sec.)	Ratio of killed insects (%)	Relative effectiveness according to comparison in concentration	
				Concentration corresponding to the effectiveness of 0.6% allethrin*	Effectiveness ratio
Compound	Concentration (%)			Concentration (%)	
<i>dl</i> -Cis-isomer of compound (1)	0.15	11'00"	65	0.2	3.00
	0.3	8'12"	84		
	0.6	6'30"	100		
Control <i>dl</i> -Trans-isomer of compound (1)	0.15	12'48"	31	0.305	1.97
	0.3	9'42"	67		
	0.6	7'18"	90		
<i>d</i> -Cis-isomer of compound (1)	0.15	7'12"	87	0.066	9.10
	0.3	5'36"	98		
	0.6	5'06"	100		
Control <i>d</i> -Trans-isomer of compound (1)	0.15	10'12"	75	0.15	4.00
	0.3	7'00"	95		
	0.6	5'30"	100		
<i>dl</i> -Cis-isomer of compound (3)	0.15	11'12"	62	0.207	2.90
	0.3	8'24"	80		
	0.6	6'36"	98		

(14)

TABLE 4 (Continued)

Composition		K.T. ₅₀ (min. sec.)	Ratio of killed insects (%)	Relative effectiveness according to comparison in concentration	
Compound	Concentration (%)			Concentration (%)	Effectiveness ratio
Control	0.15	12'54"	28		
<i>dl</i> -Trans-isomer of compound (3)	0.3	10'00"	65	0.33	1.82
	0.6	7'42"	87		
<i>d</i> -Cis-isomer of compound (3)	0.15	8'06"	84		
	0.3	6'18"	97	0.072	8.34
	0.6	4'42"	100		
Control	0.15	11'00"	76		
<i>d</i> -Trans-isomer of compound (3)	0.3	7'06"	90	0.177	3.39
	0.6	5'18"	100		
Control	0.15	11'36"	50		
<i>d</i> -Cis-isomer 15% <i>l</i> -Cis-isomer 15% <i>dl</i> -Trans-isomer 70% compound (1)	0.3	8'54"	78	0.237	2.53
	0.6	6'48"	95		
Control	0.15	12'00"	39		
<i>d</i> -Cis-isomer 7.5% <i>l</i> -Cis-isomer 7.5% <i>dl</i> -Trans-isomer 85% of compound (1)	0.3	9'24"	70	0.265	2.26
	0.6	7'00"	92		
Control Allethrin	0.6	9'54"	58	0.6	1.00

* A value calculated by inserting the K.T.₅₀ value of 0.6% allethrin into the concentration-K.T.₅₀ graph shown in each of Figs. 3 and 4.

The above-mentioned Experimental Examples show that when used in the form of an oil spray, the *d*-trans-chrysanthemate is most excellent in knock down effect, whereas when used in the form of mosquito coil, the *d*-cis-chrysanthemate has a particularly good knock down effect and is superior to the *d*-trans-chrysanthemate.

The fact that the *d*-cis-chrysanthemate displays a marked insecticidal effect when used in the form of a fumigant was not expected from the results of previous studies on allethrin isomers.

The esters which are used as active ingredients of insecticidal compositions within the present invention may be used alone, or may be incorporated with, as stabilizers, suitable amounts of phenol or bisphenol derivatives such as BHT, or arylamines such as phenyl- α -naphthylamine, phenyl- β -naphthylamine or a condensation product of phenetidine with acetone, whereby compositions which have been more stabilized in their insecticidal effect can be obtained. Further, the compositions may be increased in their insecticidal activity by incorporation with synergists for pyrethroid type insecticides such as α -[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyltoluene (hereinafter referred to as "piperonyl butoxide"), N-(2-ethylhexyl)-bicyclo(2,2,1)hepta-5-ene-enhydrophthalic acid-2,3-dicarboximide (hereinafter referred to as "MGK-264"), octachlorodipropyl ether (hereinafter referred to as "S-421"), IBTA, safroxane, Leathane, sulfoxide, "Sesamex" ("Sesamex" is a Registered Trade Mark).

In addition, beneficial effects can be expected by blending compositions within the present invention with other active ingredients such as, for example, pyrethrin, 5-benzyl-3-furylmethyl chrysanthemate (hereinafter referred to as "Chrysron", (registered trade mark of Sumitomo Chemical Co., Ltd.), 5-benzyl-3-furylmethyl-2',3',3'-trimethylcyclopropane-1'-carboxylate, 3-phenoxybenzyl chrysanthemate, dimethylmaleimidomethyl - 2,2,2,3, - tetramethylcyclopropane - 1 - carboxylate, 3 - phenoxybenzyl - 2',2',3',3' - tetramethylcyclopropane - 1' - carboxylate, 5 - propargylfurfuryl chrysanthemate, 5-propargylfurfuryl chrysanthemate, N-(chrysanthemoxymethyl)-3,4,5-tetrahydrophthalimide (hereinafter referred to as "phthalthrin") or similar known pyrethroid type, carbamate type, chlorine type or organophosphorus type insecticides.

Procedures for the preparation of compositions within the present invention and their effects are illustrated below with reference to examples and test examples; the scope of the present invention is not limited to these examples but is as defined in the appended claims.

Example 1.

A solution of 0.3 g of each of the *dl*- and *d*-cis-isomers of the present compounds (1), (2), (3) and (4) respectively in 5 ml of methanol is sufficiently mixed with a mosquito coil carrier 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 obtain 100 g of mosquito coils containing each of the above-mentioned compounds as an active ingredient.

The product thus obtained is optionally coloured by the addition of 0.5% of a dye such as Malachite Green, or may be incorporated with a phenol of *p*-hydroxybenzoic acid ester.

Example 2.

A solution of 0.3 g of allethronyl *d*-cis-chrysanthemate in 5 ml of methanol is treated using the same procedure as that described in Example 1 to obtain 100 g of a mosquito coil.

Example 3.

A solution in chloroform of 0.2 g of each of the *dl*- and *d*-cis-isomers of the present compounds (1) and (3) is uniformly adsorbed onto 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 piece thus treated was pasted another asbestos piece identical in size therewith, whereby each insecticidal fumigant to be heated was deposited on an electric heating plate.

As an alternative to asbestos, a fibrous carrier such as pulp sheet which is equivalent in effectiveness thereto may be used.

Example 4.

A solution of 0.3 g of allethronyl *d*-cis-chrysanthemate in chloroform is treated using the same procedure as that described in Example 3 to obtain an insecticidal fumigant.

Example 5.

A mixture comprising 0.2 g of each of a *dl*-cis-isomer of the present compound (1) and a *d*-cis-isomer of the present compound (3), 0.2 g of allethrin and 0.6 g of BHT is dissolved in 5 ml of methanol, and the resulting solution is treated in the same manner as that described in Example 1 to obtain mosquito coils containing each of the abovementioned compounds as an active ingredient.

Example 6.

A solution in 5 ml of methanol of 0.45 g of allethronyl *dl*-cis-chrysanthemate (containing 49% of *d*-cis-isomer) and 0.05 g of Chrysron is treated in the same manner as that described in Example 1, except that the amount of the wood flour in the mosquito coil carrier is varied to 9.5 g, whereby 100 g of a mosquito coil is obtained.

Example 7.

A mixture comprising 0.2 g of a *dl*-cis-isomer of the present compound (1) and 0.1 g of dimethylmaleimidomethyl-2,2,3,3-tetramethylcyclopropane-1-carboxylate is dissolved in 5 ml of methanol, and the resulting solution is treated in the same manner as that described in Example 1 to obtain a mosquito coil.

Example 8.

A solution of 0.5 g of allethronyl *dl*-cis,trans-chrysanthemate (containing 25% of *d*-cis-isomer) in 5 ml of methanol is treated in the same manner as that described in Example 1, except that the amount of the wood powder in the mosquito carrier is varied to 9.5 g, whereby 100 g of a mosquito coil was obtained.

Example 9.

A mixture comprising 0.2 g of a *dl*-cis-isomer of the present compound (3) and 0.1 g of Chrysron is dissolved in 5 ml of methanol, and the resulting solution is treated in the same manner as that described in Example 1 to obtain a mosquito coil.

Example 10.

A solution in 5 ml of methanol of 0.3 g of allethronyl *dl*-cis,trans-chrysanthemate (containing 18% of the *d*-cis-isomer) and 0.2 g of 5-propargyl furfuryl chrysanthemate is treated in the same manner as that described in Example 8 to obtain 100 g of a mosquito coil.

Example 11.

A mixture comprising 0.15 g of a *d*-cis-isomer of the present compound (1) and 0.3 g of S-421 is dissolved in chloroform, and the resulting solution is treated in the same manner as that described in Example 3 to obtain an insecticidal fumigant composition to be heated on an electric heating plate.

Example 12.

A solution in chloroform of 0.2 g of allethronyl *dl*-cis-chrysanthemate (containing 49% of the *d*-cis-isomer) and 0.1 g of 5-propargylfurfuryl chrysanthemate is treated in the same manner as that described in Example 3 to obtain a fibrous insecticidal fumigant composition to be heated on an electric heating plate.

Insecticidal effects of compositions within the present invention thus obtained 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 G of each of the mosquito coils obtained according to Examples 1, 5, 7 and 9 was ignited at both ends and placed at the centre of the bottom of the chamber, and the smoke inside the chamber was stirred by means of a battery driven small motor fan (blade diameter 13 cm). As a result, every mosquito coil knocked down more than 90% of the mosquitoes within 15 minutes and killed more than 90% of the insects by the next day.

Test Example 2.

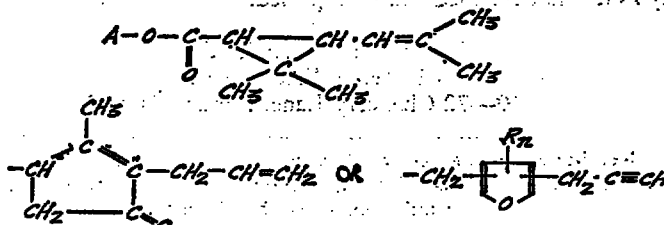
The effects on northern house mosquitoes of the mosquito coils obtained in Examples 2, 6, 8 and 10 were examined using the same procedure as that described in Test Example 1, whereby every mosquito coil knocked down more than 90% of the mosquitoes within 20 minutes and killed more than 80% of the insects by the next day.

Test Example 3.

Into a (70 cm)³ glass chamber were introduced about 50 adult northern house mosquitoes. Each of the fibrous insecticidal fumigant compositions obtained according to Examples 3, 4, 11 and 12 was put on an electric heating means, which was then placed at the centre of the bottom of the chamber. Subsequently, an electric current was applied to the heating means, and the interior of the chamber was stirred by means of a battery driven small motor fan (blade diameter 13 cm). As a result, more than 90% of the mosquitoes were knocked down within 20 minutes, and more than 80% of the knocked-down insects were killed by the next day.

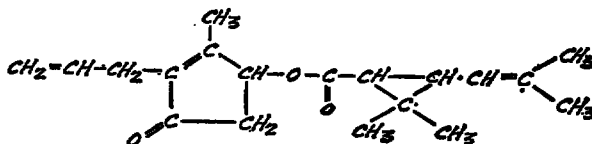
WHAT WE CLAIM IS:—

1. An insecticidal composition in the form of a fumigant comprising an inert carrier and as an essential ingredient a *d*-cis-isomer of a chrysanthemate or a mixture of isomers of a chrysanthemate which mixture contains more than 15% by weight based on the mixture of the *d*-cis-isomer, and which chrysanthemate has the formula, wherein A is

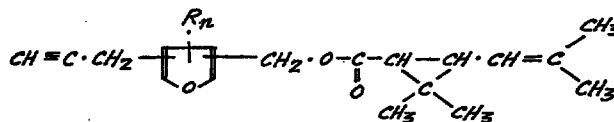


in which R is a hydrogen atom or a methyl group, and *n* is 1 or 2.

2. An insecticidal composition according to Claim 1, wherein the chrysanthemate is allethrin having the formula,

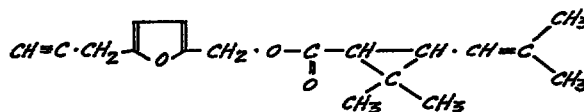


3. An insecticidal composition according to Claim 1, wherein the chrysanthemate is a compound having the formula,

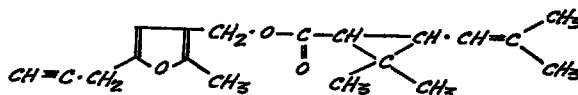


wherein R and *n* are as defined in Claim 1.

4. An insecticidal composition according to Claim 3, wherein the chrysanthemate is a compound having the formula,



5. An insecticidal composition according to Claim 3, wherein the chrysanthemate is a compound having the formula,



6. An insecticidal composition according to Claim 1, wherein the content of the *d*-cis-isomer is more than 18% by weight.

7. An insecticidal composition according to Claim 1, wherein the composition is in the form of a mosquito coil.

8. A method of killing insects, or of freeing a particular environment therefrom, which comprises exposing the insects to the vapour produced by heating an insecticidal composition according to Claim 1.



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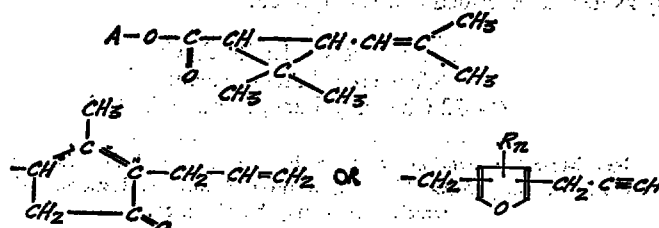
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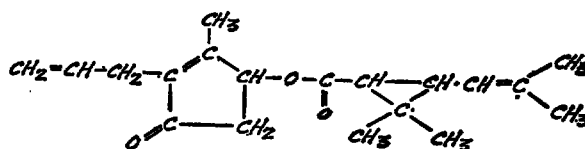
WHAT WE CLAIM IS:—

1. An insecticidal composition in the form of a fumigant comprising an inert carrier and as an essential ingredient a *d*-cis-isomer of a chrysanthemate or a mixture of isomers of a chrysanthemate which mixture contains more than 15% by weight based on the mixture of the *d*-cis-isomer, and which chrysanthemate has the formula, wherein A is

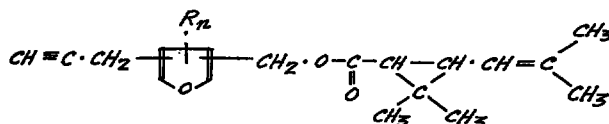


in which R is a hydrogen atom or a methyl group, and *n* is 1 or 2.

2. An insecticidal composition according to Claim 1, wherein the chrysanthemate is allethrin having the formula,

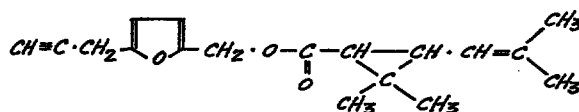


3. An insecticidal composition according to Claim 1, wherein the chrysanthemate is a compound having the formula,

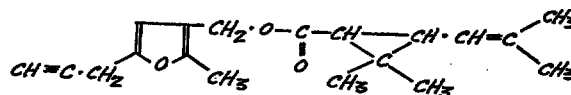


wherein R and *n* are as defined in Claim 1.

4. An insecticidal composition according to Claim 3, wherein the chrysanthemate is a compound having the formula,



5. An insecticidal composition according to Claim 3, wherein the chrysanthemate is a compound having the formula,



6. An insecticidal composition according to Claim 1, wherein the content of the *d*-cis-isomer is more than 18% by weight.

7. An insecticidal composition according to Claim 1, wherein the composition is in the form of a mosquito coil.

8. A method of killing insects, or of freeing a particular environment therefrom, which comprises exposing the insects to the vapour produced by heating an insecticidal composition according to Claim 1.



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9. Insecticidal compositions containing the *d*-cis-isomers of chrysanthemates or mixtures of isomers of chrysanthemates which mixtures contain more than 15% by weight of the *d*-cis-isomers and which are of the formula given and defined in claim 1, and which chrysanthemates are specifically disclosed herein.

10. Insecticidal compositions according to claim 1 substantially as herein described with reference to the accompanying drawings.

11. Processes for preparing an insecticidal composition according to claim 1 substantially as herein described and exemplified.

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70—72 Chancery Lane, London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.