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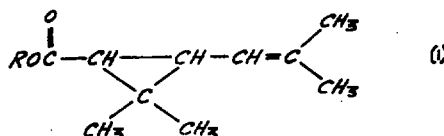
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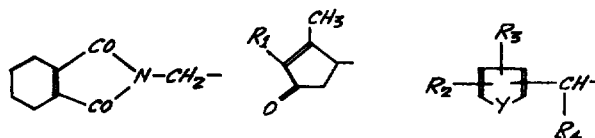
(54) INSECTICIDAL COMPOSITIONS CONTAINING (+)-CIS,
 TRANS CHRYSANTHEMATES

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation organised under the laws of Japan, of 5 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:—

The present invention relates to an insecticidal composition containing, as an active ingredient, a first component (a), given and defined below, or a mixture containing a said first component (a) and a second component (b). The first component (a) consists of one or more (+)-cis, trans-chrysanthemates, the or each said (+)-cis, trans-chrysanthemate having a (+)-cis, trans-chrysanthemic acid moiety consisting of from 10 to 30% by weight of (+)-cis-chrysanthemic acid and from 70 to 90% by weight of (+)-trans-chrysanthemic acid, and the or each said (+)-cis, trans-chrysanthemate, being independently of the formula,



wherein R is



in which R_1 is an allyl or propargyl group, R_2 is a propargyl, benzyl or phenoxy group, R_3 is optionally present and is a methyl group, R_4 is a hydrogen atom or an ethynyl group and Y is an oxygen atom or the $-\text{CH}=\text{CH}-$ group. Such a (+)-cis, trans-chrysanthemate can be prepared by esterifying a new chrysanthemic acid obtained by our new method and having an isomer ratio different from that of a conventional chrysanthemic acid, namely that given and defined above, and having no (–)-cis, trans-chrysanthemic acid, with an alcohol of the formula (II) as shown hereinafter. The second component (b) consists of one or more compounds, the or each said compound being a chrysanthemate of the formula (I), given and defined in claim 1, but having a value of R different from the value of R in the or any of each said (+)-cis, trans chrysanthemate of component (a) and having a (+)-cis, trans ratio in the total amount of its chrysanthemic acid moiety different from that in component (a).

The present invention provides an insecticidal composition which can be used for sanitary purposes, in household horticulture, agriculture, and in woods or forests, which insecticidal composition contains and inert carrier and, as an active ingredient, a component (a), given and defined above, the or each said (+)-

cis, trans-chrysanthemic acid ester being obtainable by esterifying a (+)-cis, trans-chrysanthemic acid of a new isomer ratio as defined above in the said component (a) with an alcohol of the formula,



wherein R is as defined above.

The present invention also provides an insecticidal composition which can be particularly effective because of a synergistic action which we have found to be obtained by mixing a component (a) with a component (b), as defined above. Such an insecticidal composition contains a mixture of components (a) and (b) as an active ingredient, and an inert carrier.

The (+)-cis, trans-chrysanthemates of the component (a) may, of course, be prepared by other methods than than given above, and may be prepared by merely mixing (+)-cis- and (+)-trans-chrysanthemates, which have been prepared independently, to the desired ratio.

Various types of chrysanthemate whose acid moiety is an isomer mixture of chrysanthemic acids have been used as insecticides, and the acid which has been prepared by the conventional industrial methods most readily and cheaply, and used widely in preparing insecticides is ($\pm$)-cis, trans-chrysanthemic acid.

As an alternative, (+)-trans-chrysanthemic acid is known to give esters thereof of high insecticidal activity, and insecticides having a (+)-trans-chrysanthemic acid moiety are also about to be used in practice, but the (+)-trans chrysanthemic acid is prepared using a method which includes optical resolution of a racemate and this method is found to be industrially uneconomical.

We have made a study of the synergistic action on the insecticidal activity obtained by mixing esters of each isomer in different proportions, and found surprisingly that mixing of a (+)-trans-form, which alone is found to have the highest insecticidal activity among the individual isomers, with a (+)-cis-form within a range between 7:3 and 9:1, respectively, of (+)-trans-form to (+)-cis-form ratio by weight, most preferably 8:2, has a remarkable synergistic effect. For use in practice, the insecticidal compositions of the present invention, containing the components (a) or (a) and (b) in admixture were formulated into a composition containing 0.05 to 90% by weight of active ingredient. In addition, we have found that contamination of component (a) with (–)-isomers of the chrysanthemic acid moiety, i.e. the (–)-trans- or (–)-cis-form thereof gives an adverse effect on insecticidal activity rather than giving no effect on its activity. As mentioned hereinbefore, the removal of the said (–)-isomers from the said (+)-isomers contaminated with the said (–)-isomers is found to have a large significance in the biological activity, a fact which does not appear to have been previously disclosed in the literature. Furthermore, it was found that a mixed preparation described above containing the component (a) consisting of the (+)-isomers given and defined above, and the component (b) consisting of other chrysanthemates, also shows a remarkable synergistic effect.

We have found, as a result of a study of the preparation of (+)-cis, trans-chrysanthemic acid, the following new method of preparation thereof.

That is, when ($\pm$)-cis, trans-chrysanthemic acid having a particular cis/trans isomer ratio is converted to a particular amine salt thereof, and then subjected to an optical resolution in a polar solvent e.g. chloroform or ethanol, then a mixed chrysanthemic acid containing both the cis- and trans-forms can be obtained from the crystallized salt, the cis- and trans-form both being exclusively of the (+)-, namely dextrorotatory type. In addition the ratio of cis-form to trans-form remains substantially unchanged before and after the optical resolution, when the optical resolution is carried out under suitable conditions. Furthermore, it was unexpectedly found that, when the crystallization is carried out with stirring, both the (+)-cis- and the (+)-trans-type acids have a higher optical purity than that of a (+)-trans-form obtained from a ($\pm$)-trans-form alone under the same conditions of optical resolution. Thus, the industrial optical resolution of a ($\pm$)-cis, trans chrysanthemic acid can be carried out more easily than that of a ($\pm$)-trans-acid by such a process which includes forming the amine thereof which process appears to be the first process by which optical resolution of a cis, trans-mixed chrysanthemic acid has become possible.

Optically active organic bases which can be used in such a process include (+)- α -phenyl- β -p-tolyethylamine, (+)- α -p-tolyl- β -phenyl-ethylamine, and (+)- α -phenyl- β -phenyl-ethylamine.

The above optical resolution method can be carried out effectively using a ($\pm$)-mixed-chrysanthemic acid having a ($\pm$)-cis-chrysanthemic acid content of 3% by weight, and the effectiveness of the process is increased with an increase of ($\pm$)-cis-chrysanthemic acid content. In general, the optical resolution can be carried out using a ($\pm$)-mixed-chrysanthemic acid containing more than 3% by weight thereof of ($\pm$)-cis acid, and it is particularly advantageous to carry out the process using a ($\pm$)-mixed-acid in an amount within a range of from 10 to 30% by weight of solvent in a suitable solvent, e.g. methanol, ethanol, propanol, acetone, methyl ethyl ketone or a mixture thereof with water.

Thus, using the above process, it is possible to carry out the resolution of optical isomers of ($\pm$)-cis, trans chrysanthemic acid more readily, and more advantageously and economically when applying the process industrially to give the desired product in a higher yield, than when obtaining a (+)-trans-chrysanthemic acid or a (+)-cis, trans-chrysanthemic acid by known processes.

(+)-Cis, trans-chrysanthemates incorporated in compositions within the present invention preferably have an acid moiety whose cis-form to trans-form ratio is 2:8. Examples of (+)-cis, trans-chrysanthemates which can be incorporated in compositions within the present invention are as follows, but the present invention is not limited to compositions containing such (+)-cis,trans chrysanthemates.

Compound (1); N-(3,4,5,6-tetrahydrophthalimide)-methyl-(+)-cis, trans-chrysanthemate.

Compound (2); ($\pm$)-2-allyl-3-methylcyclopent-2-ene-1-one-4-yl-(+)-cis, trans-chrysanthemate.

Compound (3); ($\pm$)-2-propargyl-3-methylcyclopent-2-ene-1-one-4-yl-(+)-cis, trans-chrysanthemate.

Compound (4); (+)-2-allyl-3-methylcyclopent-2-ene-1-one-4-yl-(+)-cis, trans-chrysanthemate.

Compound (5); (+)-2-propargyl-3-methylcyclopent-2-ene-1-one-4-yl-(+)-cis, trans-chrysanthemate.

Compound (6); 5-propargylfurfuryl-(+)-cis, trans-chrysanthemate.

Compound (7); 5-phenoxy-furfuryl-(+)-cis, trans-chrysanthemate.

Compound (8); 5-benzyl-3-furymethyl-(+)-cis, trans-chrysanthemate.

Compound (9); 5-propargyl-2-methyl-3-furymethyl-(+)-cis, trans-chrysanthemate.

Compound (10); ($\pm$)-5-propargyl- α -ethynyl-furfuryl-(+)-cis, trans-chrysanthemate

Compound (11); 3-benzylbenzyl-(+)-cis, trans-chrysanthemate.

Compound (12); 3-phenoxybenzyl-(+)-cis, trans-chrysanthemate.

A remarkable synergistic effect is found to be obtained when incorporating in an insecticidal composition

1) a mixture of (+)-cis and (+)-trans isomers of a single chrysanthemate having a value of R as previously defined, the chrysanthemate having a chrysanthemic acid moiety consisting of a mixture of cis and trans isomers in the weight ratio as previously defined which insecticidal composition contains a component (a) alone, which component (a) comprises one chrysanthemate, or

2) a mixture of chrysanthemates, each chrysanthemate having a different value of R as previously defined and having a chrysanthemic acid moiety consisting of a mixture of cis and trans isomers in the weight ratio as previously defined, which insecticidal composition contains a component (a) alone, which component (a) comprises two or more chrysanthemates, or

3) a mixture consisting of a component (a) and a component (b) as previously defined.

Insecticidal compositions within the present invention, hereinafter called "the present compositions", containing the above component (a) or a mixture of components (a) and (b) as active ingredient, have a wide range of uses as very valuable insecticides, since they have an immediate effect, strong insecticidal activity and low toxicity to mammals, in controlling harmful insanitary insects, and insects harmful to agricultural crops, household horticultural plants, stored cereals, and trees in woods or forests.

The present compositions can be used without problems, particularly owing to their low toxicity to mammals, for protecting agricultural crops against damage by insects before harvest, in greenhouse cultivation, household horticulture and food-packaging. Mixed preparations having a synergistic effect and which thus

show a particularly high insecticidal activity contain 0.2 to 90% by weight of two or more active ingredients, one of which is a component (a) which is one or more chrysanthemates having a chrysanthemic acid moiety of the abovementioned cis/trans ratio, and the or another of which is a component (b) which is one or more other chrysanthemate components, (a) and (b) being present in the proportion of 10:2—50, preferably 10:2.5—40 respectively.

The preparation of the (+)-cis, trans-chrysanthemic acids incorporated in compositions within the present invention will now be illustrated with reference to the following Examples.

Example 1.

35.2 Grams of (+)-cis, trans-chrysanthemic acid chloride containing 18.8% by weight of (+)-cis-chrysanthemic acid chloride were dissolved in 90 ml of toluene. The solution was added to a mixture of 33.2 g of N-(3,4,5,6-tetrahydrophthalimide)-methylalcohol, 21.7 g of pyridine and 180 ml of toluene over a period of 45 minutes while keeping the reaction temperature at from 30 to 35°C. The resulting solution was kept at the same temperature for a further 5 hours.

On completion of the reaction, the reaction mixture was washed three times with three portions of 150 ml of a 10% hydrochloric acid, and then with 300 ml of an 1% aqueous sodium hydroxide solution, 300 ml of water and 300 ml of a saturated sodium chloride solution in this order. The toluene layer thus obtained was dried over anhydrous magnesium sulfate, and 33 g of alumina and 16 g of silica gel were added to the solution, which was then stirred for 30 minutes at room temperature. After removing alumina and silica gel by filtration, the solution was concentrated under a reduced pressure to give 56.7 g of N-(3,4,5,6-tetrahydrophthalimide)-methyl-(+)-cis, trans-chrysanthemate as an oil.

$$[\alpha]_D^{25} = -15.13^\circ \text{ [CHCl}_3\text{]C} = 4.15\%; n_D^{28} = 1.5182$$

Example 2.

29.2 Grams of (+)-cis, trans-chrysanthemic acid chloride containing 17.7% by weight of (+)-cis-chrysanthemic acid chloride were dissolved in 30 ml of toluene. The solution was added to a mixture of 25.0 g of (±)-2-allyl-3-methylcyclopent-2-ene-1-one-4-ol, 18.6 g of pyridine and 40 ml of toluene over a period of 30 minutes while keeping the reaction temperature at from 40 to 50°C. The solution was kept at the same temperature for a further 4 hours.

Thereafter, the reaction solution was treated in the same manner as that described in Example 1 to give 45.8 g of (+)-2-allyl-3-methylcyclopent-2-ene-1-one-4-yl-(+)-cis, trans-chrysanthemate as an oil.

$$[\alpha]_D^{25} = +3.12^\circ \text{ [CHCl}_3\text{]C} = 7.6\%; n_D^{28} = 1.5050$$

Example 3.

61.7 Grams of (+)-cis, trans-chrysanthemate acid chloride containing 18.7% by weight of (+)-cis-chrysanthemic acid chloride were dissolved in 170 ml of toluene. The solution was added to a mixture of 58.1 g of 5-benzyl-3-furylmethylalcohol, 36.6 g of pyridine and 185 ml of toluene over a period of 2 hours while keeping the reaction temperature at from 25 to 30°C. The solution was kept at the same temperature for a further 5 hours. Thereafter, the reaction solution was treated in the same manner as that described in Example 1 to give 105.4 g of 5-benzyl-3-furylmethyl-(+)-cis, trans-chrysanthemate as an oil.

$$[\alpha]_D^{25} = -2.45^\circ \text{ [CHCl}_3\text{]C} = 3.3\%; n_D^{28} = 1.5290$$

Example 4.

A solution of 56.8 g of 5-propargylfuryl alcohol dissolved in 157.8 g of toluene was cooled to below 10°C, and 63.3 g of triethylamine were added thereto. The mixture was cooled again to below 10°C, and a solution of 81.8 g of (+)-cis, trans-chrysanthemic acid chloride containing 19.0% by weight of (+)-cis-chrysanthemic acid chloride in 186.8 g of toluene was added thereto at a temperature of below 40°C. The mixture was maintained at from 35 to 40°C for a further 3 hours. Thereafter, the reaction solution was treated in the same manner as that described in Example 1 to give 105 g of 5-propargylfuryl-(+)-cis, trans-chrysanthemate as oil.

$$[\alpha]_D^{24} = -17.54^\circ \text{ [CHCl}_3\text{]C} = 20.5\%; n_D^{21.5} = 1.5076$$

Example 5.

A mixture of 25.7 g of (+)-cis, trans-chrysanthemic acid chloride containing 15.2% of (+)-cis-chrysanthemic acid chloride, and 80 ml of toluene was cooled to from -20° to -25°C , and 15.9 g of triethylamine were then added thereto at the same temperature. After stirring for 15 minutes at the same temperature, a solution of 21.0 g of 5-propargyl- α -ethynylfurfuryl alcohol in 20 ml of toluene was added dropwise thereto.

After addition, the mixture was gradually allowed to cool at room temperature, and maintained at from 20 to 25°C while stirring.

Thereafter, the solution was treated in the same way as that described in Example 1 to give 40.9 g of 5-propargyl- α -ethynylfurfuryl-(+)-cis, trans-chrysanthemate as an oil.

$$[\alpha]_D^{24} = -7.57^\circ \text{ [CHCl}_3\text{]C} = 5.81\%; n_D^{28} = 1.5098$$

Example 6.

85.0 Grams of (+)-cis, trans-chrysanthemic acid chloride containing 16.0% by weight of (+)-cis-chrysanthemic acid chloride were dissolved in 270 ml of toluene. The solution was added to a mixture of 86.75 g of 3-phenoxybenzyl alcohol, 51.4 g of pyridine and 270 ml of toluene over a period of 1 hour while keeping the reaction temperature at from 20 to 30°C . The solution was maintained at the same temperature for a further 4 hours. Thereafter, the reaction solution was treated in the same way as that described in Example 1 to give 148.5 g of 3-phenoxybenzyl-(+)-cis, trans-chrysanthemate as an oil.

$$[\alpha]_D^{27} = -6.43^\circ \text{ [CHCl}_3\text{]C} = 9.672\%; n_D^{28} = 1.5048$$

Example 7.

18.7 Grams of (+)-cis, trans-chrysanthemic acid chloride containing 19.0% by weight of (+)-cis-chrysanthemic acid chloride were dissolved in 20 ml of toluene. The solution was added to a mixture of 16.0 g of (+)-2-allyl-3-methylcyclopent-2-ene-1-one-4-ol, 11.9 g of pyridine and 30 ml of toluene over a period of 30 minutes while maintaining the reaction temperature at from 40 to 50°C . The solution was maintained at the same temperature for a further 4 hours. Thereafter the reaction solution was treated in the same manner as that described in Example 1 to give 29.4 g of (+)-2-allyl-3-methylcyclopent-2-ene-1-one-4-yl-(+)-cis, trans-chrysanthemate as an oil.

$$[\alpha]_D^{22} = -23.01^\circ \text{ [n-Hexane]C} = 1.069\%; n_D^{28} = 1.5098$$

Example 8.

11 Grams of (+)-cis, trans-chrysanthemic acid chloride containing 19% by weight of (+)-cis-chrysanthemic acid chloride were dissolved in 30 ml of toluene. The solution was added to a mixture of 8 g of (+)-2-propargyl-3-methylcyclopent-2-ene-1-one-4-ol, 5.6 g of pyridine and 50 ml of toluene over a period of 1 hour while keeping the reaction temperature at from 20 to 30°C . The solution was maintained at the same temperature for a further 6 hours. Thereafter, the reaction solution was treated in the same manner as that described in Example 1 to give 6 g of ($\pm$)-2-propargyl-3-methylcyclopent-2-ene-1-one-4-yl-(+)-cis, trans-chrysanthemate as an oily matter.

$$n_D^{22} = 1.5199.$$

Insecticidal compositions within the present invention will now be illustrated with reference to the following Test Examples, for the purpose of illustrating the excellent properties of the present insecticidal compositions, and the outstanding synergistic effect which can be obtained.

- 1) when using a composition containing, as component (a) a mixture of isomers of a single chrysanthemate as previously defined,
- 2) when using a composition containing, as component (a), two chrysanthemates each with an acid moiety consisting of a mixture of cis and trans isomers as previously defined, and
- 3) when using a composition containing a component (a) in admixture with a

component (b), each as previously defined.

Test Example 1.

The synergistic action obtained by including a chrysanthemate having (+)-cis chrysanthemic acid moiety in a mixture with a chrysanthemate having the same alcohol moiety but having a (+)-trans acid moiety was investigated for a series of chrysanthemates, each of which contains, as an alcohol moiety one of N-(3,4,5,6-tetrahydropthalimide)-methylol, 5-benzyl-3-furylmethylol, 3-phenoxybenzyl-alcohol, (+)-2-allyl-3-methylcyclopent-2-ene-1-one-4-ol or (+)-2-allyl-3-methylcyclopent-2-ene-1-one-4-ol. The (+)-cis- and the (+)-trans-type esters were each independently formulated into oil sprays thereof as shown in the following Table 1 using deodorized kerosene. 5 Ml of one of each of the oil sprays formulated was sprayed, using Campbell's turn table apparatus ["Soap and Sanitary Chemicals", Vol. 14, No. 6, 119 (1938)]. A shutter was opened for 20 seconds after spraying, and about 100 house-fly adults (*Musca domestica*) per group were exposed to the descending mist for 10 minutes, and then transferred to an observation cage. In the cage, the flies were fed and allowed to stand for one day at room temperature. Thereafter, the number of flies killed was counted to calculate the % mortality.

The values of LC_{50} (50% lethal concentration) are shown in Table 1 and the attached Fig. 1.

From Table 1 and Fig. 1, it can clearly be seen that the (+)-trans-chrysanthemate mixed with a small amount of (+)-cis-chrysanthemate shows a higher insecticidal activity than either the (+)-trans form alone (which has the highest activity among the known esters), and that the synergistic effect is particularly remarkable at a cis-form to trans-form ratio of 2:8.

TABLE 1

Samples to be tested		LC ₅₀ (mg/100 ml)	Relative efficacy taken as 100
N-(3,4,5,6-tetrahydrophthalimide)-methyl-(+)(1:1)-cis, trans(3:7)-chrysanthemate		175	taken as 100
"	-(+)-trans-chrysanthemate	80	219
"	-(+)-cis-chrysanthemate	627	28
"	-(+)-cis, trans(4:6)-chrysanthemate	104	168
"	-(+)-cis, trans(3:7)-chrysanthemate	68	258
"	-(+)-cis, trans(2:8)-chrysanthemate	61	287
5-benzyl-3-furylmethyl-(-)(1:1)-cis, trans(3:7)-chrysanthemate		19	taken as 100
"	-(+)-trans-chrysanthemate	10	190
"	-(+)-cis-chrysanthemate	54	35
"	-(+)-cis, trans(4:6)-chrysanthemate	15	127
"	-(+)-cis, trans(3:7)-chrysanthemate	8.7	218
"	-(+)-cis, trans(2:8)-chrysanthemate	7.4	257

TABLE 1 (Continued)

Samples to be tested		LC ₅₀ (mg/100 ml)	Relative efficacy taken as 100
3-phenoxybenzyl-(±)(1:1)-cis, trans(3:7)-chrysanthemate		50	taken as 100
„	-(+)-trans-chrysanthemate	23	217
„	-(+)-cis-chrysanthemate	29	172
„	-(+)-cis, trans(4:6)-chrysanthemate	24	208
„	-(+)-cis, trans(3:7)-chrysanthemate	19	263
„	-(+)-cis, trans(2:8)-chrysanthemate	16	312
(±)-2-allyl-3-methylcyclopent-2-ene-1-one-4-yl-(±)(1:1)-cis, trans(3:7)-chrysanthemate		170	taken as 100
„	-(+)-trans-chrysanthemate	82	207
„	-(+)-cis-chrysanthemate	178	96
„	-(+)-cis, trans(4:6)-chrysanthemate	93	183
„	-(+)-cis, trans(3:7)-chrysanthemate	70	243
„	-(+)-cis, trans(2:8)-chrysanthemate	64	266

TABLE 1 (Continued)

Samples to be tested	LC ₅₀ (mg/100 ml)	Relative efficacy taken as 100
(+)-2-allyl-3-methylcyclopent-2-ene-1-one-4-yl-(±)(1:1)-cis, trans(3:7)-chrysanthemate	88	taken as 100
„ -(-)-trans-chrysanthemate	43	205
„ -(-)-cis-chrysanthemate	95	93
„ -(-)-cis, trans(4:6)-chrysanthemate	53	166
„ -(-)-cis, trans(3:7)-chrysanthemate	37	239
„ -(-)-cis, trans(2:8)-chrysanthemate	31	284
5-propargyl-furfuryl-(±)(1:1)-cis, trans(3:7)-chrysanthemate	97	taken as 100
„ -(-)-trans-chrysanthemate	49	198
„ -(-)-cis-chrysanthemate	67	145
„ -(-)-cis, trans(4:6)-chrysanthemate	54	180
„ -(-)-cis, trans-(3:7)-chrysanthemate	43	226
„ -(-)-cis, trans(2:8)-chrysanthemate	37	262

Test Example 2.

In order to investigate the synergistic action of a (+)-cis- on a (+)-trans chrysanthemic acid moiety in a mixture of (+)-cis, trans (for example 2:8)-chrysanthemic acid moieties of a chrysanthemate and the synergistic action between such a chrysanthemate (as a component (a) as previously defined) and a different type of chrysanthemate (as a component (b) as previously defined) in a present composition, the two chrysanthemate components were formulated into aerosols as shown in the following Table 2 by the method of Preparation 10 described hereinafter.

Each aerosol consisted of one of a series of insecticidal compositions each containing

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- 1) a component (a) alone, which component (a) comprises a mixture of (+)-cis, trans chrysanthemates (i.e. two values of R),
- 2) a mixture of components (a) and (b), or
- 3) a single chrysanthemate as control. These are designated as types 1—3 respectively in Tables 2 and 3.

It should be pointed out that some of the "control" compositions are, in fact, compositions within the present invention containing a component (a) alone, which component (a) comprises a single chrysanthemate (i.e. a single value of R as previously defined). The "control" compositions were, however, employed in this Test Example, at lower concentrations of from 0.1% to 0.4% (for direct comparison with the concentrations at which the mixed chrysanthemates were used) than would, in practice, be employed where a composition contains only a single chrysanthemate. Even from a comparison of the results obtained by the various "control" compositions at these lower concentrations, it can be seen that those control compositions within the present invention are more effective than those outside the invention.

The insecticidal activity of each aerosol on house-fly adults (*Musca domestica*) was then tested by an aerosol test method using a (6 ft)³ Peet Grady's chamber [the method disclosed in "Soap and Chemical Specialities, Blue Book" (1965)]. The results are shown in Tables 2 and 3.

A synergistic effect in compositions within the present invention can clearly be observed from Table 2, considering that each mixed preparation has a higher insecticidal activity than the total activity obtained by the addition of the activity of each insecticidal component constituting the preparation when used alone and this is so whether the activity of each insecticidal component independently is based on the same concentration at which each component alone is present in the composition containing the mixture, or whether it is based on the total concentration of all components of the mixture of the preparation. The following Table 3 also illustrates the same synergistic effects.

TABLE 2

The figures in parentheses indicate Compound Nos. of the present invention.

Type of Composition	Contents of Composition (Aerosols)	Knock-down ratio (%)			Mortality (%)
		5'	10'	15'	
1	[(1)-cis, trans 2:8-0.2%]+[(4)-cis, trans 2:8-0.1%]	47	75	100	78
2	[(1) " " " " +[(4)-(+)-trans alone-0.1%]	45	72	100	73
1	[(1) " " " " +[(6)-cis, trans 2:8-0.1%]	34	68	100	100
2	[(1) " " " " +[(6)-(-)-trans alone-0.1%]	25	59	98	98
2	[(1) " " " " +[(6)-(+)(1:1)-cis, trans(3:7)-0.1%]	20	50	91	87
1	[(1) " " " " +[(12)-cis, trans 2:8-0.1%]	27	42	93	85
1	[(2)-cis, trans 2:8-0.2%]+[(6)-cis, trans 2:8-0.1%]	31	63	99	98
2	[(2) " " " " +[(6)-(+)-trans alone-0.1%]	23	57	96	96
2	[(2) " " " " +[(6)-(+)(1:1)-cis, trans(3:7)-0.1%]	19	48	90	85
1	[(2) " " " " +[(12)-cis, trans 2:8-0.1%]	25	39	87	80

TABLE 2 (Continued)

Type of Composition	Contents of Composition (Aerosols)		Knock-down ratio (%)			Mortality (%)
			5'	10'	15'	
2	[(12) cis, trans 2:8-0.1%]-[(1)-(-)-trans alone 0.2%]		20	36	89	77
2	[(12) +[(1)-(-) (1:1)-cis, trans (3:7)-0.2%]		14	30	68	50
2	[(12) -[(2)-(+)-trans alone-0.2%]		16	32	84	70
2	[(12) -[(4)-(+)-trans alone-0.1%]		24	46	87	83
3	[(1) cis, trans 2:8 0.2%]		15	29	58	16
3	[(1) .. 0.3%]		19	34	68	20
3	[(2) .. 0.2%]		14	28	50	15
3	[(2) .. 0.3%]		19	31	63	19
3	[(4) .. 0.1%]		13	29	52	16
3	[(4) .. 0.2%]		17	35	70	28
3	[(4) .. 0.3%]		20	43	82	39
3	[(6) .. 0.1%]		7	20	32	32
3	[(6) .. 0.2%]		12	37	70	68
3	[(6) .. 0.3%]		18	53	81	81
3	[(8) .. 0.2%]		12	22	49	20
3	[(8) .. 0.3%]		15	28	59	32
3	[(8) .. 0.4%]		19	33	67	48
	Control (used in the form of single compound)					

TABLE 2 (Continued)

Type of Composition	Contents of Composition (Acrosols)	Knock-down ratio (%)				Mortality (%)
		5'	10'	15'		
3	[(12) cis, trans 2.8 0.1%]	0	6	17	17	
3	[(12) " 0.2%]	3	15	35	31	
3	[(12) " 0.3%]	5	19	41	38	
3	[(1)-(+)-trans alone 0.2%]	12	20	49	13	
3	[(1)-(-)-trans alone 0.3%]	15	25	55	15	
3	[(1)-(+)(1:1)-cis, trans (3:7) 0.2%]	7	18	37	10	
3	[(1)-(+)(1:1)-cis, trans (3:7) 0.3%]	10	21	56	14	
3	[(1)-(+)(1:1)-cis, trans (3:7) 0.4%]	15	39	75	18	
3	[(2)-(+)-trans alone 0.2%]	10	21	43	12	
3	[(2)-(+)-trans alone 0.3%]	13	28	54	18	
3	[(4)-(+)-trans alone 0.1%]	8	20	42	10	
3	[(4)-(-)-trans alone 0.2%]	12	30	61	24	
3	[(4)-(-)-trans alone 0.3%]	18	37	75	34	
3	[(6)-(+)-trans alone 0.1%]	4	19	28	28	
3	[(6)-(+)-trans alone 0.2%]	7	36	59	57	
3	[(6)-(+)-trans alone 0.3%]	10	47	76	75	
3	[(6)-(+)(1:1)-cis, trans (3:7) 0.1%]	2	9	19	19	
3	[(6)-(+)(1:1)-cis, trans (3:7) 0.2%]	4	19	47	44	
3	[(6)-(+)(1:1)-cis, trans (3:7) 0.3%]	7	26	60	58	

Control
(used in
the form
of single
compound)

TABLE 3

The figures in parentheses indicate Compound Nos. of the present invention.
Each chrysanthemate (except the (+) cis, trans compositions) given below has a cis, trans ratio of 2:8.

Type of Composition	Contents of Composition (Aerosols)	Knock-down ratio (%)			Mortality (%)
		5'	10'	15'	
1	[(3) 0.2%] + [(6) 0.1%]	34	65	100	100
1	" + [(12) 0.1%]	27	48	94	88
1	[(5) 0.1%] + [(12) 0.1%]	27	59	89	88
1	[(7) 0.1%] + [(1) 0.2%]	28	44	94	84
1	" - [(2) 0.2%]	27	42	90	78
1	[(9) 0.2%] + [(1) 0.2%]	40	64	100	60
1	" - [(2) 0.2%]	41	62	100	56
1	" + [(6) 0.1%]	28	53	90	90
1	" - [(12) 0.1%]	20	37	82	75
1	[(10) 0.2%] + [(1) 0.2%]	45	76	100	72
1	" + [(2) 0.2%]	43	72	100	70
1	" + [(6) 0.1%]	35	69	100	100
1	" + [(12) 0.1%]	33	54	98	98
2	" + [(6)-(+) (1:1-cis, trans (3:7) 0.1%]	27	53	99	99

TABLE 3 (Continued)

Type of Composition	Contents of Composition (Aerosols)	Knock-down ratio (%)			Mortality (%)
		5'	10'	15'	
1	[(11) 0.1%]+[(2) 0.2%]	19	42	85	60
3	Control (used in the form of single compound)	17	32	53	18
3		15	29	50	15
3		1	8	19	18
3		10	21	46	19
3		15	30	64	27
3		0	5	15	15
3		15	29	58	16
3		14	28	50	15
3		7	20	32	32
3		2	9	19	19
3		0	6	17	17
		[(3) 0.2%]			
	[(5) 0.1%]				
	[(7) 0.1%]				
	[(9) 0.2%]				
	[(10) 0.2%]				
	[(11) 0.1%]				
	[(1) 0.2%]				
	[(2) 0.2%]				
	[(6) 0.1%]				
	[(6)-(±) (1:1)-cis, trans (3:7)-0.1%]				
	[(12) 0.1%]				

Test Example 3.

In the same manner as that described in Test Example 2, in order to investigate each of the synergistic actions referred to in Test Example 2, a series of insecticidal compositions were formulated into mosquito coils shown in the following Table 4.

0.8 Gram of each mosquito coil was burnt in a (6 ft)³ Peet Grady's Chamber which was used for the aerosol test in Example 2. Thereafter, 50 northern house mosquito adults (*Culex pipens pullens*) per group were introduced to the smoke, and the number of knocked down adults with lapse of time was counted. The values of KT₅₀ (a period required for 50% knock-down), the periods required for 80% knock-down, and the durations of activity are summarized in Table 4 and Table 5, in which the type of insecticide is given as in Tables 2 and 3.

The types of composition numbered 1—3 are as for Test Example 2.

Again, as in Test Example 2, although some of the "control" compositions were compositions within the present invention containing as a component (a) a single chrysanthemate, the concentration, of from 0.05% to 0.4%, at which the control compositions were employed is a very low concentration at which the compounds would not, in practice, be used independently.

From Table 4, the same synergistic effect of a composition within the present invention as that obtained when formulating such a composition into an aerosol can be observed. The following Table 5 shows this same effect.

As clearly shown in the results of Test Example 2 (Tables 2 and 3) and Test Example 3 (Tables 4 and 5), each mixed preparation within the present invention shows a remarkable synergistic effect due to mixing, compared with the activity of the respective insecticidal components alone constituting the preparation.

TABLE 4

The figures in parentheses indicate Compound Nos. of the present invention.

Type of Composition	Content of Composition (mosquito coil)	KT ₅₀ (min)	80% Knock-down ratio	
			Time required (min)	Duration (min)
1	[(2) 0.2%]+[(6) 0.1%]	8	29	>91
2	„ +[(6), (+)-trans 0.1%]	8.4	33	>87
2	„ +[(6), (±)-cis, trans 0.1%]	13	53.4	>66.6
1	„ +[(12) 0.05%]	10.4	53	>67
1	„ +[(12) 0.1%]	8.5	32.4	>87.6
1	„ +[(12) 0.2%]	6.2	26.1	>93.9
2	„ +[(12), (+)-trans 0.1%]	9.1	40.2	>79.8
2	„ +[(12), (±)-cis, trans 0.2%]	8.8	35.2	>84.8
1	[(4) 0.2%]+[(8) 0.1%]	4.8	26	>94
1	„ +[(12) 0.1%]	4	17	>103
2	[(6) 0.1%]+[(2), (+)-trans 0.2%]	8	30	>90
2	„ +[(2), (+)-cis, trans 0.3%]	10.2	50	>70
2	[(8) 0.1%]+[(4), (+)-trans 0.1%]	6	32	>88
2	[(12) 0.1%]+[(2), (+)-trans 0.2%]	8.9	36.5	>83.5
2	„ +[(2), (+)-cis, trans 0.3%]	9.5	46	>74

TABLE 4 (Continued)

Type of Composition	Content of Composition (mosquito coil)		KT ₅₀ (min)	80% Knock-down ratio	
				Time required (min)	Duration (min)
3	Control (used in the form of single compound)	[(2) 0.2%]	21	>120	—
"		[(2) 0.25%]	15.2	>120	—
"		[(2) 0.3%]	9.3	80	>40
"		[(2) 0.4%]	8	29	>91
"		[(4) 0.2%]	8.7	32	>88
"		[(4) 0.3%]	6.2	28	>92
"		[(6) 0.1%]	90	>120	—
"		[(6) 0.3%]	30	40	>80
"		[(6) 0.4%]	22	35	>85
"		[(8) 0.1%]	>120	>120	—
"		[(8) 0.3%]	11.5	85	>35
"		[(12) 0.05%]	>120	>120	—
"		[(12) 0.1%]	72	>120	—
"		[(12) 0.2%]	43	70	>50
"		[(12) 0.25%]	40	61	>59
"		[(12) 0.3%]	35.5	50	>70
"		[(12) 0.4%]	30.2	42	>78
3	Control (used in the form of the single compound)	[(2), (+)-trans 0.2%]	25.4	>120	—
"		[(2), (+)-trans 0.3%]	11.5	85.5	>34.5
"		[(2), (±)-cis, trans 0.3%]	>120	>120	—
"		[(2), (±)-cis, trans 0.4%]	29.5	>120	—
"		[(4), (+)-trans 0.1%]	26	>120	—
"		[(4), (+)-trans 0.2%]	9.2	40	>80
"		[(6), (+)-trans 0.1%]	94	>120	—
"		[(6), (+)-trans 0.3%]	41	68	>52
"		[(6), (±)-cis, trans 0.1%]	>120	>120	—
"		[(6), (±)-cis, trans 0.3%]	71	110	>10
"		[(12), (+)-trans 0.1%]	82	>120	—
"		[(12), (+)-trans 0.3%]	49	78	>42

TABLE 4 (Continued)

Type of Composition	Content of Composition (mosquito coil)	KT ₅₀ (min)	80% Knock-down ratio	
			Time required (min)	Duration (min)
„	[(12), (±)-cis, trans 0.2%]	79	>120	—
„	[(12), (±)-cis, trans 0.4%]	57	85	>35

TABLE 5

The figures in parentheses indicate Compound Nos. of the present invention.

Type of Composition	Content of Composition (mosquito coil)	KT ₅₀ (min)	80% Knock-down ratio	
			Time required (min)	Duration (min)
1	[(3) 0.2%]+[(6) 0.1%]	8.2	28	>92
2	„ +[(6), (+)-trans 0.1%]	8.6	35	>85
2	„ +[(6), (±)-cis, trans 0.1%]	12.8	51.3	>68.7
1	„ +[(12) 0.1%]	8	25	>95
1	[(8) 0.2%]+[(6) 0.1%]	7.7	28	>92
2	„ +[(6), (+)-trans 0.1%]	8.5	39	>81
2	„ +[(6), (+)-cis, trans 0.1%]	9	47.9	>72.1
1	„ +[(12) 0.1%]	7.5	25	>95
2	„ +[(12), (+)-trans 0.1%]	7.9	30.2	>89.8
1	[(9) 0.2%]+[(6) 0.1%]	8	31.3	>88.7
2	„ +[(6), (+)-trans 0.1%]	8.6	33.5	>86.5
2	„ +[(6), (±)-cis, trans 0.1%]	9.3	46	>74
1	„ +[(12) 0.1%]	7.7	29.3	>90.7
2	[(6) 0.1%]+[(3), (+)-trans 0.2%]	8.5	34.5	>85.5
2	„ +[(3), (±)-cis, trans 0.3%]	10.5	37	>83.3
2	„ +[(8), (+)-trans 0.2%]	8	29.7	>90.3
2	„ +[(8), (±)-cis, trans 0.3%]	9.2	34.1	>85.9
2	[(6) 0.1%]+[(9), (+)-trans 0.2%]	8.8	32.8	>87.2
2	„ +[(9), (±)-cis, trans 0.3%]	8.2	31.4	>88.6

TABLE 5 (Continued)

Type of Composition	Content of Composition (mosquito coil)		KT ₅₀ (min)	80% Knock-down rate		
				Time required (min)	Duration (min)	
2	[(12) 0.1%]+[(3), (+)-trans	0.2%	8.3	31.7	>88.3	
2	„ +[(3), (±)-cis, trans	0.3%	10.2	36.6	>83.4	
2	„ +[(8), (+)-trans	0.2%	7.8	27.4	>92.6	
2	„ +[(8), (±)-cis, trans	0.3%	8.9	30.3	>88.7	
2	„ +[(9), (+)-trans	0.2%	7.9	30.6	>89.4	
2	„ +[(9), (±)-cis, trans	0.3%	8.1	32.3	>87.7	
3	Control	[(3)	0.2%	21	>120	—
„		[(8)	0.2%	12.2	85	>35
„		[(9)	0.2%	15	>120	—
„		[(6)	0.1%	90	>120	—
„		[(12)	0.1%	72	>120	—
„		[(3), (+)-trans	0.2%	24.7	>120	—
„		[(3), (+)-cis, trans	0.3%	>120	>120	—
„		[(6), (+)-trans	0.1%	94	>120	—
„		[(6), (±)-cis, trans	0.1%	>120	>120	—
3		[(8), (+)-trans	0.2%	14.8	>120	—
„		[(8), (±)-cis, trans	0.3%	50.7	>120	—
„		[(9), (+)-trans	0.2%	18.2	>120	—
„		[(9), (±)-cis, trans	0.3%	58.5	>120	—
„		[(12), (+)-trans	0.1%	82	>120	—

In the preparation of insecticidal compositions within the present invention, the abovementioned component (a) or mixture of components (a) and (b), hereinafter called "the present components", may be formulated, like pyrethroids, into any desired form, for example, an oil spray, emulsifiable concentrate, dust, aerosol, wettable powder, granulate, mosquito coil, fumigant effective with or without heating, bait or luring dust or other solid preparation, by any well known method, using auxiliary agents and/or carriers, as are used for common insecticidal compositions.

Furthermore, the present components may be increased in their insecticidal activity when used in combination with a known synergist for pyrethroids such as α -[2-(2-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyltoluene (referred to as "piperonylbutoxide"), 1,2-methylenedioxy-4-[2-(octylsulfinyl)propyl]-benzene (referred to as "sulfoxide"), 4-(3,4-methylenedioxyphenyl)-5-methyl-1,3-dioxane (referred to as "safroxane"), N-(2-ethylhexyl)bicyclo[2.2.1]hepta-5-ene-2,3-dicarboximide (referred to as "MGK-264"), octachlorodipropylether (referred to as "S-421"), or isobornylthiocyanacetate (referred to as "Thanite"), or with other known synergists for allethrin or pyrethrin.

Although chrysanthemate type compounds are generally a little inferior in their resistance to light, heat and oxidation than other compounds used as insecticides, the present components can be formulated into insecticidal compositions having a more stable activity by incorporating therein, as a stabilizing agent, a requisite amount of an antioxidant, or U.V. absorber, for example a phenol derivative (e.g. BHT or BHA), a bisphenol derivative, an arylamine derivative, (e.g. phenyl- α -naphthylamine, phenyl- β -naphthylamine) or a condensation product resulting from phenetidine and acetone, or a benzophenone compound.

In addition, the present components may be formulated into multi-purpose compositions of high activity by incorporating other active ingredients, for example, organochlorine type insecticides, e.g., DDT, BHC, and methoxychlor; organophosphorus type insecticides, e.g., O,O-dimethyl-O-(3-methyl-4-nitrophenyl)-phosphorothioate (referred to as "Sumithion", a registered Trade Mark of Sumitomo Chemical Co., Ltd.), and O,O-dimethyl-O-(2,2-dichlorovinyl)phosphate (referred to as "DDVP"); carbamate type insecticides, e.g. 1-naphthyl-N-methylcarbamate, 3,4-dimethylphenyl-N-methylcarbamate, and 3,5-dimethylphenyl-N-methylcarbamate; other insecticides; microbial insecticides, e.g., B.T. and B.M. fungicides; nematocides; acaricides; herbicides; fertilizers; insect hormone compounds; or other agricultural chemicals. Furthermore, a synergistic effect can also be expected of a combination of the present components with at least some of the above active ingredients.

The preparation and activity of compositions within the present invention will be illustrated with reference to the following Preparation Examples and subsequent Examples, which are given for the purpose of illustration, and do not limit the scope of the present invention. In the Preparation Examples and subsequent Examples parts and percentages are by weight unless otherwise stated.

Preparation Example 1.

(Type 1 Composition).

To 0.05 part of one of each of the compounds (1), (2), (3), (4), (7), (8), (9), (10) and (11) was added 0.1 part of the compound (6). The mixtures were each dissolved in kerosene to 100 parts of total weight. Ten oil sprays were thus obtained.

Preparation Example 2.

(Type 1 Composition).

To 0.1 part of one of each of the compounds from (1) to (10) was added 0.1 part of the compound (12). The mixtures were each dissolved in kerosene to 100 parts of total weight. Ten oil sprays were thus obtained.

Preparation Example 3.

(Type 1 Composition).

To 10 parts of one of each of the compounds (4), (5), (6), (10), (11) and (12) were added 5 parts of the compound (2), 30 parts of safroxane, 10 parts of Sorpol SM—200 (registered trade name for an emulsifier sold by Toho Kagaku Co., Ltd.) and 45 parts of xylene. The mixtures were each thoroughly mixed to make a solution. Six emulsifiable concentrates were thus obtained.

Preparation Example 4.

(Type 2 Composition).

To 20 parts of one of each of the compounds (1), (2), (6) and (12) were added 5 parts of 5-propargyl-2-methyl-3-furylmethyl-($\pm$)-cis,trans-chrysanthemate, 5 parts of Sorpos SM—200 (the same as above) and 70 parts of 300 mesh talc. The mixtures were each thoroughly mixed by means of a mortar. Four wettable powders were thus obtained.

Preparation Example 5.

(Type 2 Composition).

To 1 part of one of each of the compounds (1), (2), (6) and (12) were added 1 part of 5-propargyl- α -ethynyl-furfuryl-($\pm$)-cis,trans-chrysanthemate and 2 parts of piperonyl-butoxide. The mixtures were each dissolved in 20 parts of acetone, and 96 parts of 300 mesh diatomaceous earth were added thereto. The resulting mixtures were each thoroughly mixed by means of a mortar, and the acetone was then removed by evaporation. Four dusts were thus obtained.

Preparation Example 6.

(Type 1 Composition).

0.1 Gram of one of each of the compounds (5), (6), (7), (8), (9), (10) and (12), 0.3 g of the compound (2) and 0.2 g of BHT were dissolved in 20 ml. of methanol. Each of the solution were uniformly mixed with 99.4 g of a mosquito coil carrier containing Tabu powder, Pyrethrum marc and wood powder in a ratio of 3:5:1, and the methanol was then evaporated. Each residue was mixed with 150 ml of water, kneaded thoroughly, shaped into a mosquito coil and dried. Seven mosquito coils were thus obtained.

Preparation Example 7.

(Type 2 Composition).

0.2 Gram of one of each of the compounds (2), (4), (6), (9) and (13), 0.2 g of BHT and 0.2 g of 5-propargylfurfuryl-(±)-cis,trans-chrysanthemate were dissolved in 20 ml of methanol. The solutions were each treated in the same way as that described in Preparation Example 6 to give a mosquito coil.

Preparation Example 8.

(Type 1 Composition).

0.1 Gram of one of each of the compounds (2), (3), (4), (8) and (9), 0.05 g of the compound (12), 0.1 g of BHT and 0.1 g of piperonyl-butoxide were dissolved in a requisite amount of chloroform. The solutions were each adsorbed uniformly on to the surface of an asbestos piece of 3.5 cm x 1.5 cm in area and 0.3 mm in thickness, and then another piece of asbestos of the same size was adhered to the surface thereof. Five fibrous fumigant insecticidal compositions effective on heating for use in conjunction with a heater were thus obtained. A pulp plate may be used in place of asbestos as a fibrous carrier having the same effect.

Preparation Example 9.

(Type 2 Composition).

0.05 Gram of one of each of the compounds (1), (2), (4), (6), (11) and (12), 0.05 g of 5-propargyl-2-methyl-3-furymethyl-(±)-cis,trans-chrysanthemate, 0.2 g of BHT, and 0.05 g of piperonyl-butoxide were dissolved in a requisite amount of chloroform. The solutions were each treated in the same manner as that described in Preparation Example 8 to give a fibrous fumigant insecticidal composition effective on heating for use in conjunction with a heater.

Preparation Example 10.

(Type 2 Composition).

0.2 Part of the compound (1), 0.1 part of the compound (12), and 0.1 part of 5-propargyl-α-ethynyl-furfuryl-(+)-trans-chrysanthemate were dissolved in a mixture of 7 parts of xylene and 7.6 parts of deodorized kerosene. The solution was introduced into an aerosol container. After attaching a valve portion to the container, 85 parts of propellant (e.g. liquefied petroleum gas) were charged therein under pressure through the valve. An aerosol was thus obtained.

Preparation Example 11.

(Type 2 Composition).

0.2 Part of the compound (2), 0.2 part of 3-phenoxybenzyl-(±)-cis,trans-chrysanthemate, and 0.4 part of piperonyl-butoxide were dissolved in a mixture of 7 parts of xylene and 7.2 parts of deodorized kerosene. The solution was treated in the same manner as that described in Preparation Example 10 to give an aerosol.

Preparation Example 12.

(Type 2 Composition).

0.2 Part of the compound (1), 0.5 part of a pyrethrin extract containing 20% of pyrethrin, and 0.1 part of 3-phenoxybenzyl-(+)-trans-chrysanthemate were dissolved in a mixture of 7 parts of xylene and 7.2 parts of deodorized kerosene. The solution was treated in the same manner as that described in Preparation Example 10 to give an aerosol.

Preparation Example 13.

(Type 1 Composition).

0.2 Part of the compound (1), 0.05 part of the compound (2), and 0.5 part of Sumithion were dissolved in a mixture of 7 parts of xylene and 7.25 parts of

deodorized kerosene. The solution was treated in the same manner as that described in Preparation Example 10 to give an aerosol.

Preparation Example 14.
(Type 1 Composition).

5 3 Parts of the compound (6), 1 part of the compound (9), 1 part of 3,4-
dimethylphenyl-N-methylcarbamate, 5 parts of Toyolignin CT (registered trade
name of Toyo Spinning Co., Ltd.) and 90 parts of GSM clay (registered trade name
for clay sold by Zieklite Mining Co. Ltd.) were thoroughly mixed by means of a
10 mortar.

 The mixture was then well mixed with 10% by its weight of water, granulated
by means of a granulator and air-dried to give a granular preparation. 10

 The insecticidal activity of the present compositions thus obtained is
illustrated by the following Examples.

Example 9.

15 5 Milliliters of one of each of the oil sprays formulated according to
Preparation Example 1 were sprayed, using Campbell's turn table method (the
same as above). About 100 house-fly adults (*Musca domestica*) per group were
exposed to the descending mist for 10 minutes. By the next day, more than 80% of
the flies were killed with each oil spray. 15

Example 10.

20 Groups each of about 50 northern house mosquito adults (*Culex pipens pullens*)
were introduced into a series of (70 cm)³ glass chambers, one group in each chamber.
0.7 Milliliter of one of each of the oil sprays formulated according to Preparation
Example 2 was sprayed under a pressure of 20 lb/in² through a glass atomizer, one
25 into each chamber. More than 80% of the adults were knocked down within 10
minutes. By the next day, more than 80% of the mosquitoes were killed with each
oil spray. 25

Example 11.

30 The emulsifiable concentrates formulated according to Preparation Example
3 were each diluted 50,000 times with water. 2 Litres of each test emulsion so
prepared were poured, one each into a series of styrene cases of 23 cm x 30 cm in
area and 6 cm in depth, and about 100 full grown larvae of the northern house
mosquito (*Culex pipens pullens*) were introduced into each cage. By the next day,
more than 90% of the larvae were killed with each concentrate. 30

Example 12.

35 Groups each of about 50 northern house mosquito adults (*Culex pipens pullens*)
were introduced into a series of (70 cm)³ glass chambers in each of which a battery-
type small fan (wing diameter 13 cm) was set and run, each chamber containing
one group of mosquitoes. 0.1 Gram of one of each of the mosquito coils
40 formulated according to Preparation Examples 6 and 7 was ignited at both ends
and placed one in each chamber. More than 80% of the adults were knocked down
within 20 minutes with each mosquito coil. By the next day, more than 80% of the
adults were killed. 40

Example 13.

45 Groups, each of about 50 house-fly adults (*Musca domestica*) were introduced
into a series of (70 cm)³ glass chambers in each of which a battery-type small fan
(wing diameter 13 cm) was set and run, each chamber containing one group of
flies. One of each of the fumigant compositions formulated according to
Preparation Examples 8 and 9 was placed on a heater located in each chamber and
50 heated. More than 80% of the adults were knocked down within 20 minutes with
each fumigant. 50

Example 14.

55 The insecticidal activity on house-fly adults (*Musca domestica*) of the aerosols
formulated according to Preparation Examples 10, 11, 12 and 13 was tested by the
aerosol test method (the same as above) using a (6 ft)³ Peet Grady's chamber. The
results are as shown in Table 6. 55

TABLE 6

Composition	Knock-down ratio (%)			Mortality (%)
	5 min.	10 min.	15 min.	
Aerosol (Preparation 10)	39	60	100	100
„ („ 11)	27	54	97	97
„ („ 12)	38	67	98	85
„ („ 13)	35	69	100	100

Example 15.

Each of a series of glass Petri dishes, each of 14 cm in inside diameter, was coated on its inside wall with butter, leaving at the lower part an uncoated portion of 1 cm in height. On to the bottom of each dish, one of each of the dusts formulated according to Preparation Example 5 was uniformly dusted in a proportion of 2 g/cm².

Subsequently, groups each containing 10 German cockroach adults (*Blattella germanica*) per group were introduced into the dishes, one group in each dish, and allowed to come into contact with the dust for 30 minutes. After three days, more than 70% of the knocked down adults were killed.

Example 16.

In 1/50,000 Wagner pots were grown rice plants which had been left for 45 days after sowing. The wettable powders formulated according to Preparation Example 4 were each diluted 500 times with water. Each test solution so prepared was individually sprayed on the rice plants in a proportion of 10 ml per pot. Each pot was covered with wire net and about 30 adult green rice leaf-hoppers (*Nephotettix cincticeps*) were introduced into the pot. After 1 day, more than 80% of the hoppers were killed.

Example 17.

Each of the emulsifiable concentrates formulated according to Preparation Example 3 was diluted 100 times with water. Groups each of about 10 third to fourth instar larvae of the tobacco cut worm (*Spodoptera litura*) were introduced into a series of glass Petri dishes, each of 14 cm in inside diameter, and containing one group per dish and 1 ml of one of each of the dilute solutions was sprayed into each dish. Thereafter, the larvae in each group were fed and allowed to stand in another dish, and after two days more than 90% of the larvae were killed with each concentrate.

Example 18.

Aliquots of 10 litres of water were each poured into one of a series of 14-l polypropylene buckets, and 1 g of one of each of the granular preparations formulated according to Preparation Example 14 was placed in each bucket. After one day, about 100 full grown northern house mosquito larvae (*Culex pipens pullens*) were immersed in the water. More than 90% of the larvae were killed within 24 hours.

WHAT WE CLAIM IS:—

1. An insecticidal composition containing as an active ingredient, one or more (+)-cis, trans chrysanthemates, the or each said (+)-cis, trans chrysanthemate independently having a chrysanthemic acid moiety consisting of from 10 to 30% by weight of (+)-cis- and from 70 to 90% by weight of (+)-trans-chrysanthemic acid and the or each said (+)-cis, trans-chrysanthemate being independently of the formula,

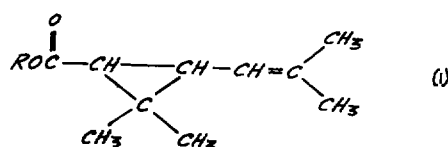




TABLE 6

Composition	Knock-down ratio (%)			Mortality (%)
	5 min.	10 min.	15 min.	
Aerosol (Preparation 10)	39	60	100	100
„ („ 11)	27	54	97	97
„ („ 12)	38	67	98	85
„ („ 13)	35	69	100	100

Example 15.

Each of a series of glass Petri dishes, each of 14 cm in inside diameter, was coated on its inside wall with butter, leaving at the lower part an uncoated portion of 1 cm in height. On to the bottom of each dish, one of each of the dusts formulated according to Preparation Example 5 was uniformly dusted in a proportion of 2 g/cm².

Subsequently, groups each containing 10 German cockroach adults (*Blattella germanica*) per group were introduced into the dishes, one group in each dish, and allowed to come into contact with the dust for 30 minutes. After three days, more than 70% of the knocked down adults were killed.

Example 16.

In 1/50,000 Wagner pots were grown rice plants which had been left for 45 days after sowing. The wettable powders formulated according to Preparation Example 4 were each diluted 500 times with water. Each test solution so prepared was individually sprayed on the rice plants in a proportion of 10 ml per pot. Each pot was covered with wire net and about 30 adult green rice leaf-hoppers (*Nephotettix cincticeps*) were introduced into the pot. After 1 day, more than 80% of the hoppers were killed.

Example 17.

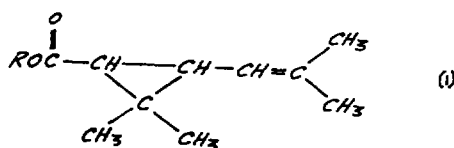
Each of the emulsifiable concentrates formulated according to Preparation Example 3 was diluted 100 times with water. Groups each of about 10 third to fourth instar larvae of the tobacco cut worm (*Spodoptera litura*) were introduced into a series of glass Petri dishes, each of 14 cm in inside diameter, and containing one group per dish and 1 ml of one of each of the dilute solutions was sprayed into each dish. Thereafter, the larvae in each group were fed and allowed to stand in another dish, and after two days more than 90% of the larvae were killed with each concentrate.

Example 18.

Aliquots of 10 litres of water were each poured into one of a series of 14-l polypropylene buckets, and 1 g of one of each of the granular preparations formulated according to Preparation Example 14 was placed in each bucket. After one day, about 100 full grown northern house mosquito larvae (*Culex pipens pullens*) were immersed in the water. More than 90% of the larvae were killed within 24 hours.

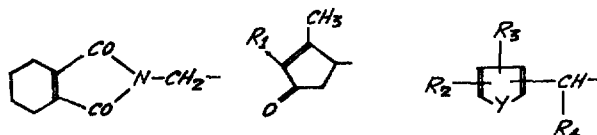
WHAT WE CLAIM IS:—

1. An insecticidal composition containing as an active ingredient, one or more (+)-cis, trans chrysanthemates, the or each said (+)-cis, trans chrysanthemate independently having a chrysanthemic acid moiety consisting of from 10 to 30% by weight of (+)-cis- and from 70 to 90% by weight of (+)-trans-chrysanthemic acid and the or each said (+)-cis, trans-chrysanthemate being independently of the formula,





wherein R is a radical of the formula,



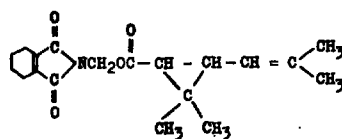
in which R_1 is an allyl or propargyl group, R_2 is a propargyl, benzyl or phenoxy group, R_3 is optionally present and is a methyl group, R_4 is a hydrogen atom or an ethynyl group, and Y is the group $-\text{CH}=\text{CH}-$ or an oxygen atom, and an inert carrier.

2. An insecticidal composition according to claim 1 containing two different said (+)-cis, trans chrysanthemates.

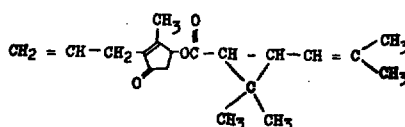
3. An insecticidal composition according to claim 1 or claim 2, containing 0.05 to 90% by weight of the said active ingredient.

4. An insecticidal composition according to claim 1, claim 2 or claim 3, containing one or more said (+)-cis, trans-chrysanthemates of the formula (I) the or each said chrysanthemic acid moiety thereof consisting of 20% by weight of (+)-cis- form and 80% by weight of (+)-trans-form thereof.

5. An insecticidal composition according to any one of the preceding claims wherein the or one said (+)-cis,trans-chrysanthemate is a compound of the formula,

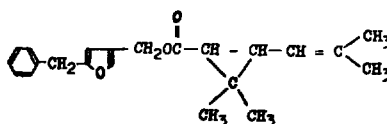


6. An insecticidal composition according to any one of Claims 1 to 4, wherein the or one said (+)-cis,trans-chrysanthemate is a compound of the formula,

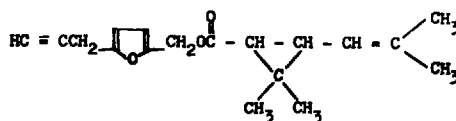


7. An insecticidal composition according to any one of Claims 1 to 4, wherein the or one said (+)-cis,trans-chrysanthemate is ($\pm$)- or (+)-2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl-(+)-cis,trans-chrysanthemate.

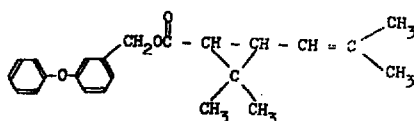
8. An insecticidal composition according to any one of Claims 1 to 4, wherein the or one said (+)-cis,trans-chrysanthemate is a compound of the formula,



9. An insecticidal composition according to any one of Claim 1 to 4, wherein the or one said (+)-cis,trans-chrysanthemate is a compound of the formula,



10. An insecticidal composition according to any one of claims 1 to 4 wherein the or one said (+)-cis,trans-chrysanthemate is a compound of the formula,



11. An insecticidal composition containing an inert carrier and, as active ingredients,

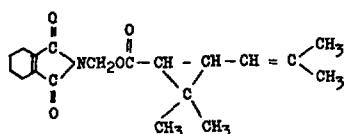
a component (a) consisting of the said active ingredient given and defined in claim 1, and

a component (b) consisting of one or more compounds, the or each said compound being a chrysanthemate of the formula (I), given and defined in claim 1, but having a value of R different from the value of R in the or any of each said (+)-cis, trans chrysanthemate of component (a) and having a (+)-cis, trans ratio in the total amount of its chrysanthemic acid moiety different from that in component (a).

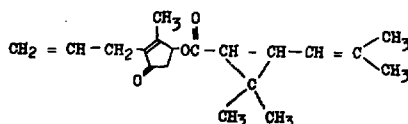
12. An insecticidal composition according to claim 11, wherein the ratio of the weight of component (a) to that of component (b) is from 10:2 to 10:50 inclusive.

13. An insecticidal composition according to claim 11 or claim 12, wherein the said composition contains from 0.2 to 90% inclusive by weight of the active ingredient.

14. An insecticidal composition according to claim 11, claim 12, or claim 13, wherein the or one said (+)-cis, trans-chrysanthemate of component (a) is a compound of the formula,

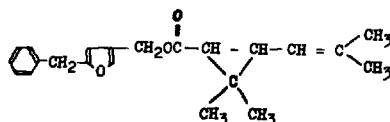


15. An insecticidal composition according to Claim 11, Claim 12 or Claim 13, wherein the or one said (+)-cis,trans-chrysanthemate of the component (a) is a compound of the formula,

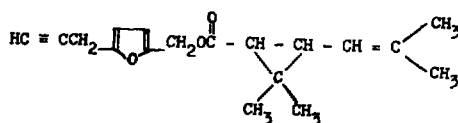


16. An insecticidal composition according to Claim 11, Claim 12 or Claim 13, wherein the or one said (+)-cis,trans-chrysanthemate of the component (a) is (±)- or (+)-2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl-(+)-cis,trans-chrysanthemate.

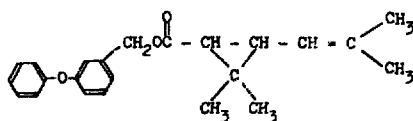
17. An insecticidal composition according to Claim 11, Claim 12 or Claim 13, wherein the or one said (+)-cis,trans-chrysanthemate of the component (a) is a compound of the formula,



18. An insecticidal composition according to Claim 11, Claim 12 or Claim 13, wherein the or one said (+)-cis,trans-chrysanthemate of the component (a) is a compound of the formula,



19. An insecticidal composition according to claim 11, claim 12 or claim 13, wherein the or one said (+)-cis,trans-chrysanthemate of the component (a) is a compound of the formula,



20. A method of killing insects, which includes contacting the insects with an insecticidal composition according to any one of Claims 1 to 10.

5 21. A method of killing insects, which includes contacting the insects with an insecticidal composition according to any one of Claims 11 to 19.

22. An insecticidal composition according to claim 1 or claim 11 substantially as herein described and exemplified.

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MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70—72 Chancery Lane,
London, WC2A 1AD.
Agents for the Applicants.