

# PATENT SPECIFICATION

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## (54) INSECTICIDAL COMPOSITIONS

(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 containing an inert carrier and, as active ingredient, a mixture of N-(3,4,5,6-tetrahydrophthalimido) - methyl chrysanthemate [hereinafter referred to as "the compound (1)"] which is a known chrysanthemic acid ester type insecticide, or 2-allyl-3-methyl-cyclopent-2-ene-1-one-4-yl chrysanthemate [hereinafter referred to as "the compound (2)"] which is a known chrysanthemic acid ester type insecticide of allethrolon, and 3 - phenoxybenzyl - 2',2' - dimethyl - 3'-(2'',2'' - dichlorovinyl) cyclopropanecarboxylate [hereinafter referred to as "the compound (3)"] which is an ester disclosed in recently published U.K. specification 1413491. Compositions within the present invention, which can be prepared merely by mixing the abovementioned compounds with each other, are extremely high in insecticidal effect and extremely useful, since the disadvantages of using any of the individual compounds alone have been overcome by using such a mixture and since the effects thereof have been synergistically increased.

The present invention also provides a method of knocking down or killing insects which comprises contacting the insects with the abovementioned insecticidal composition.

The composition preferably contains from 0.05 to 90% by weight of the said active ingredient, and the weight ratio of compound (1) or (2) to compound (3) in the said mixture is preferably in a range of from 1:9 to 9:1 inclusive.

The compounds (1) and (2) are both currently available insecticides each of which displays an extremely quick knock-down effect against harmful insanitary insects, e.g. houseflies, mosquitoes and cockroaches, and insects

harmful to agricultural crops, examples of which insects are green rice leafhoppers, and these compounds are found to have the most rapid knock-down effect of the natural and synthetic chrysanthemic acid ester type compounds. However, when either of the compounds (1) or (2) is used alone, it is not always high in its killing effect and hence it is sometimes required to be incorporated with a piperonyl butoxide synergist or an insecticide high in killing effect.

We have conducted extensive studies in an attempt to overcome the disadvantages of using the compound (1) or (2) while retaining the merits of such use. As a result, we have found that when the compound (1) or (2) is mixed with a suitable amount of the compound (3), the resulting mixture exhibits a synergistic insecticidal activity and displays surprising effects, which could not have been anticipated from the effects of the individual compounds when used alone, and is sufficiently low in toxicity to mammals as to be usable in practice.

The synergistic effect exhibited by compositions within the present invention is illustrated in more detail below with reference to Experimental Examples in which all parts and percentages are by weight unless otherwise stated. The compounds (1), (2) and (3) all have isomers thereof derived at least from the acid residues thereof, and compositions containing mixtures of compound (1) or (2) with compound (3) are of course, all within the scope of the present invention irrespective of the particular isomers present.

In the accompanying drawings, Fig. 1 is a graph showing the relation between mixing ratio of compound (1) to compound (3) by weight, against knock-down ratio and mortality, and illustrates the insecticidal effect on adult houseflies of an insecticidal composition containing the (±)-trans isomer (referring to the acid residue) of the compounds (1) and (3); Fig. 2 is a graph showing the relation between mixing ratio of a compound (2) to compound (3) by weight, against knock-down ratio and mortality, and illustrates the insecticidal effect on adult houseflies of an

insecticidal composition containing an isomer of the compound (2) consisting of ( $\pm$ )-allethrolon- and the (+)-trans-acid residue and an isomer of the compound (3) containing a ( $\pm$ )-cis,-trans acid residue; and Fig. 3 is a graph showing the relation between mixing ratio of compound (2) to compound (3) by weight, against knock-down ratio and mortality, and illustrates the insecticidal effect on adult houseflies of an insecticidal composition containing an isomer of compound (2) consisting of (+)-allethrolon- and (+)-trans acid residue and an isomer of the compound (2) containing a ( $\pm$ )-cis, trans acid residue.

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#### Experimental Example 1.

The compounds and mixtures thereof shown in Table 1 were individually formu-

lated using deodorized kerosene into 0.1% oil preparations.

Groups each of about 50 adult houseflies per group were introduced into respective glass chambers each of (70 cm)<sup>3</sup> and then sprayed with 0.7 ml. of one of each of the abovementioned oil preparations under a pressure of 1.5 kg/cm<sup>2</sup> using a glass atomizer. Thereafter, the number of knocked down houseflies was counted and the value of KT<sub>50</sub> (50% knock-down time) calculated. After 10 minutes, the knocked down houseflies were collected and allowed to stand for a day in an observation cage with feeding, and the numbers of alive and dead houseflies were then counted to determine the % mortality. The results obtained are as shown in Table 1.

Table 1

| 0.1% Oil preparation                                                                            | Knock-down effect      |                 | Mortality (%) |
|-------------------------------------------------------------------------------------------------|------------------------|-----------------|---------------|
|                                                                                                 | KT <sub>50</sub> (sec) | Ratio of effect |               |
| ( $\pm$ )-Trans acid isomer of compound (1)                                                     | 106                    | 100             | 26            |
| " (3)                                                                                           | 455                    | 23              | 73            |
| ( $\pm$ )-Trans acid isomer of compound (1) + ( $\pm$ )-Trans acid isomer of compound (3) (9:1) | 103                    | 103             | 48            |
| " (8:2)                                                                                         | 96                     | 110             | 70            |
| " (5:5)                                                                                         | 92                     | 115             | 96            |
| " (2:8)                                                                                         | 141                    | 75              | 90            |
| " (1:9)                                                                                         | 216                    | 49              | 81            |
| Pyrethrin                                                                                       | 143                    | 74              | 23            |

As can be seen from the above Table 1 and from Fig. 1, mixtures of the compounds (1) and (3), particularly the 9:1 to 2:8 mixtures, exhibit an excellent synergistic effect.

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#### Experimental Example 2.

The compounds and mixtures thereof shown in Table 2 were individually formulated using deodorized kerosene into 0.2% oil preparations. Groups each of about 50 adult houseflies per group were introduced into respective glass chambers each of (70 cm)<sup>3</sup>

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and then sprayed with 0.7 ml. of one of each of the abovementioned oil preparations under a pressure of 1.5 kg/cm<sup>2</sup> using a glass atomizer. Thereafter, the number of knocked down houseflies was counted and the value of KT<sub>50</sub> calculated. After 10 minutes, the knocked down houseflies were collected and allowed to stand for a day in an observation cage with feeding, and the numbers of alive and dead houseflies were counted to determine the % mortality. The results obtained are as shown in Table 2.

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Table 2

| 0.2% Oil preparation                                                                                          | Knock-down effect      |                 | Mortality (%) |
|---------------------------------------------------------------------------------------------------------------|------------------------|-----------------|---------------|
|                                                                                                               | KT <sub>50</sub> (sec) | Ratio of effect |               |
| (±)-Allethrolon-(+)-trans-acid isomer (hereinafter referred to as "(±)-lon-(+)-trans isomer") of compound (2) | 125                    | 100             | 23            |
| (±)-Allethrolon-(+)-trans-acid isomer (hereinafter referred to as "(±)-lon-(+)-trans isomer") of compound (2) | 82                     | 153             | 36            |
| (±)-Cis, trans-acid residue (hereinafter referred to as "(±)-cis, trans isomer") of compound (3)              | 447                    | 28              | 75            |
| (±)-Lon-(+)-trans isomer of compound (2) + (±)-Cis, trans isomer of compound (3)                              | 102                    | 123             | 64            |
| "                                                                                                             | 98                     | 128             | 90            |
| "                                                                                                             | 127                    | 98              | 98            |
| "                                                                                                             | 212                    | 59              | 95            |
| "                                                                                                             | 291                    | 43              | 87            |
| (±)-Lon-(+)-trans isomer of compound (2) + (±)-Cis, trans isomer of compound (3)                              | 66                     | 190             | 75            |
| "                                                                                                             | 67                     | 187             | 93            |
| (±)-Lon-(±)-trans isomer of compound (2) + (±)-Cis, trans isomer of compound (3)                              | 83                     | 151             | 100           |
| "                                                                                                             | 156                    | 80              | 97            |
| "                                                                                                             | 246                    | 51              | 92            |

As can be seen from Figs. 2 and 3, the values of knock-down ratio and mortality of the mixtures (represented by the curved lines) are higher than those expected in theory (represented by the straight lines joining the values obtained for the respective com-

pounds alone). The graphs thus illustrate the fact that the mixtures shown a synergistic effect.

into test solutions. The test solutions were tested in their insecticidal effect by topical application method, a trace amount of one of each of the solutions being dropped onto the dorsum prothoraxes of adult German cockroaches using a microsyringe. As a result, the 50% lethal doses (LD<sub>50</sub>) of the solution measured after 72 hours were as shown in Table 3.

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- 5      **Experimental Example 3.**  
The (+)-trans isomer of the compound (1), the (±)-trans isomer of the compound (3) and the mixtures thereof shown in Table 3 were individually formulated using acetone

Table 3

| Test chemical                                                             | LD <sub>50</sub><br>(γ/Roach) | Ratio of<br>effect |
|---------------------------------------------------------------------------|-------------------------------|--------------------|
| (+)-Trans isomer of compound (1)                                          | 2.43                          | 100                |
| (±)-Trans isomer of compound (3)                                          | 0.57                          | 426                |
| (+)-Trans isomer of compound (1) ± (±)-Trans isomer of compound (3) (9:1) | 1.32                          | 184                |
| " (8:2)                                                                   | 1.05                          | 231                |
| " (5:5)                                                                   | 0.61                          | 398                |
| " (2:8)                                                                   | 0.46                          | 528                |
| " (1:9)                                                                   | 0.59                          | 412                |
| Pyrethrin                                                                 | 1.40                          | 174                |

- 20      **Experimental Example 4.**  
The (±)-Cis, trans isomers of the compounds (1) and (3) and the mixtures thereof shown in Table 4 were individually formulated by a conventional procedure into 20% emulsifiable concentrates.
- 25      Rice plants, which had been grown for about 40 days after sowing in pots, were sprayed with 10 ml/pot of a 2,000-fold dilu-

tion of one of each of the abovementioned emulsifiable concentrates. After air-drying, the rice plants were infested with adult green rice leafhoppers, and the number of knocked down leafhoppers was counted with lapse time to determine the value of KT<sub>50</sub> (time required to knock down 50% of the leafhoppers). The results obtained are as shown in Table 4.

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TABLE 4

| Emulsifiable concentrate                                                         | KT <sub>50</sub> (min) |
|----------------------------------------------------------------------------------|------------------------|
| (±)-Cis, trans isomer of compound (1)                                            | 14'                    |
| " compound (3)                                                                   | 23'                    |
| (±)-Cis, trans isomer of compound (1) + (±)-Cis, trans isomer compound (3) (8:2) | 13'                    |
| " (5:5)                                                                          | 17'                    |
| " (2:8)                                                                          | 17' 30"                |

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Experimental Example 5.

The (±)-Lon-(+)-trans isomer of the compound (2), (±)-cis, trans isomer of the compound (3), (+)-trans isomer of the compound (3) and the mixtures thereof shown in Table 5 were individually formulated in the same manner as in Formulation Example 4 described later into aerosol preparations having active ingredient concentrations as shown in Table 5.

The aerosol preparations were tested in insecticidal effect by the aerosol test method [described in "Soap & Chemical Specialties, Bluebook" (1965)], using a series of Peet Grady's chambers into each of which had been introduced a group of 100 adult houseflies. The results obtained are as shown in Table 5.

Table 5

| Aerosol                                       | Sprayed amount (g/1000ft <sup>3</sup> ) | Knock-down ratio (%) |        |        | KT <sub>50</sub> (min) |               | Mortality (%) |
|-----------------------------------------------|-----------------------------------------|----------------------|--------|--------|------------------------|---------------|---------------|
|                                               |                                         | 5 min                | 10 min | 15 min | Measured               | Theoretical*1 |               |
| (±)-Lon-(+)-trans isomer of compound (2) 0.3% | 3.2                                     | 15                   | 31     | 56     | 13.8                   | —             | 12            |
| (±)-Cis, trans isomer of compound (3) 0.3%    | 3.2                                     | 4                    | 22     | 53     | 14.8                   | —             | 52            |
| (+)-Trans isomer of compound (3) 0.3%         | 3.1                                     | 9                    | 30     | 67     | 12.4                   | —             | 76            |
| (±)-Lon-(+)-trans isomer of compound (2) 0.2% | 3.2                                     | 22                   | 64     | 81     | 8.0                    | 14.1          | 85            |
| + (±)-Cis, trans isomer of compound (3) 0.1%  |                                         |                      |        |        |                        |               |               |
| (±)-Lon-(+)-trans isomer of compound (2) 0.2% | 3.1                                     | 28                   | 79     | 92     | 6.6                    | 13.3          | 95            |
| + (+)-Trans isomer of compound (3) 0.1%       |                                         |                      |        |        |                        |               |               |

\* 1: Theoretical value calculated using the synergistic effect calculation formula of Yun-Pei Sun et al. [J. E. E., 53, pages 887-891(1960)].

Experiment Example 6.

5 The ( $\pm$ )-Lon-(+)-trans isomer of the compound (2), (+)-lon-(+)-trans isomer of the compound (2), ( $\pm$ )-cis, trans isomer of the compound (3) and the mixtures there-  
10 of shown in Table 6 were individually formulated in the same manner as that described in Formulation Example 14 described later into aerosol preparations having active ingredient concentrations as shown in Table 6.

15 Glass cylinders, each of 20 cm in diameter and 20 cm in height, were each covered at the bottom with a nylon mesh net having 16 holes per inch and coated with butter at the upper part of the inner wall, and a group of 20 adult German cockroaches was introduced to each cylinder. Each cylinder containing cockroaches was placed on top of an empty glass cylinder

of 20 cm in diameter and 20 cm in height, and another empty glass cylinder, this also being of 20 cm in diameter but 40 cm in height was placed on top of the cylinder containing the cockroaches. 20

From the top of each of the columns of glass cylinders thus produced, one of each of the aforesaid aerosol preparations was sprayed on to the cockroaches, and the number of cockroaches knocked down within 20 minutes was counted with lapse of time to determine the value of  $KT_{50}$ . After 20 minutes had elapsed from spraying, the cockroaches were allowed to stand for 3 days with feeding in a feeding dish, and the numbers of alive and dead cockroaches were counted to determine the % mortality. The results obtained are as shown in Table 6. 25 30 35



Table 7

| Mosquito coil                                 | Knock-down ratio (%) |     |     |     |     |     |      |      | KT <sub>50</sub> (min) |               |
|-----------------------------------------------|----------------------|-----|-----|-----|-----|-----|------|------|------------------------|---------------|
|                                               | 15'                  | 30' | 45' | 60' | 75' | 90' | 105' | 120' | Measured               | Theoretical*1 |
|                                               |                      |     |     |     |     |     |      |      |                        |               |
| (±)-Lon-(+)-cis, trans isomer of compound (2) | 3                    | 21  | 42  | 59  | 74  | 77  | 83   | 88   | 51                     | -             |
| (+)-Lon-(+)-cis, trans isomer of compound (2) | 10                   | 37  | 55  | 72  | 80  | 87  | 93   | 97   | 39                     | -             |
| (±)-Cis, trans isomer of compound (3)         | 0                    | 5   | 13  | 30  | 37  | 48  | 72   | 81   | 87                     | -             |
| (±)-Lon-(+)-cis, trans isomer of compound (2) | 5                    | 32  | 58  | 70  | 83  | 90  | 94   | 96   | 41                     | 59.1          |
| (+)-Cis, trans isomer of compound (3)         |                      |     |     |     |     |     |      |      |                        |               |
| (+)-Lon-(+)-cis, trans isomer of compound (2) | 19                   | 51  | 69  | 81  | 89  | 93  | 96   | 97   | 29.5                   | 47.7          |
| + (±)-Cis, trans isomer of compound (3)       |                      |     |     |     |     |     |      |      |                        |               |
| (+)-Lon-(+)-cis, trans isomer of compound (2) | 15                   | 43  | 61  | 79  | 83  | 90  | 92   | 95   | 34                     | 53.7          |
| + (±)-Cis, trans isomer of compound (3)       |                      |     |     |     |     |     |      |      |                        |               |

\*1: As previously defined.

As can be seen from the abovementioned Experimental Examples 1 to 7, insecticidal compositions within the present invention are markedly high in insecticidal effect due to the synergistic effect.

In preparing the insecticidal compositions within the present invention, the mixture comprising the active ingredient may be formulated by any of the well known procedures using diluents for general insecticides, as in the case of conventional pyrethroids, into insecticidal compositions, optionally in any conventional form, for example, as oil preparations, emulsifiable concentrates, dust preparations, aerosols, wettable powders, fine granule preparations, mosquito coils, electrical mosquito killer mats, fogging mists, fumigants effective on heating or without heating, and dust or solid preparation incorporated with baits or like substances attractive to insects.

The insecticides of the present invention can be even further enhanced in their insecticidal effect when used in admixture with synergists for pyrethroids, for example,  $\alpha$ -[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyltoluene (hereinafter referred to as "piperonyl butoxide"), 1,2-methylenedioxy-4-[2-(octylsulfinyl)propyl]benzene (hereinafter referred to as "sulfoxide"), 4-(3,4-methylenedioxyphenyl)-5-methyl-1,3-dioxane (hereinafter referred to as "Safroxane"), N-(2-ethylhexyl)-bicyclo[2,2,1]hepta-5-ene-2,3-dicarboximide (hereinafter referred to as "MGK-264"), octachlorodipropyl ether (hereinafter referred to as "S-421") and isobornyl thiocyanacetate (hereinafter referred to as "Thanite"—a registered Trade Mark), or with other known synergists effective for allethrin and pyrethrin.

In general, chrysanthemic acid ester type compounds are somewhat low in their stability to light, heat and oxidation. Accordingly, when antioxidants or ultraviolet absorbers, for example phenol derivatives, e.g. BHT (butylated hydroxytoluene) and BHA (butylated hydroxyanisole), bisphenol derivatives, arylamines, e.g. phenyl- $\alpha$ -naphthylamine, phenyl- $\beta$ -naphthylamine and phenetidine condensates, or benzophenone type compounds are added in suitable amounts as stabilizers to insecticidal compositions within the present invention, it is possible to obtain insecticidal compositions which have been more stabilized in their effectiveness.

Furthermore, insecticides within the present invention may be used in admixture with physiologically active substances, for example, organo-chlorine type insecticides, e.g. DDT, BHC and methoxychlor; organo-phosphorus type insecticides, e.g. O,O-dimethyl-O-(3-methyl-4-nitrophenyl)phosphorothioate [hereinafter referred to as "Sumithion" (registered trademark of Sumitomo Chemical Co., Ltd.)], O,O-dimethyl-O-(2,2-dichloro-

vinyl) phosphate (hereinafter referred to as "DDVP") and O,O-dimethyl-O-4-cyanophenyl phosphorothioate [hereinafter referred to as "Cyanox" (registered trademark of Sumitomo Chemical Co., Ltd.)]; carbamate type insecticides, e.g. 1-naphthyl-N-methyl carbamate, 3,4-dimethylphenyl-N-methyl carbamate, 3,5-dimethylphenyl-N-methyl carbamate and 2-isopropoxyphenyl-N-methyl carbamate; chrysanthemic acid ester type insecticides, e.g. known chrysanthemic acid esters and their isomers, or other insecticides, or with other chemicals used in agriculture, such as fungicides, nematocides, acaricides, herbicides, fertilizers, microbial pesticides, e.g. Bacillus thuringiensis preparations and Bacillus moritae preparations, and insect hormones, whereby multi-purpose compositions more enhanced in their effectiveness can be prepared.

Because of their having such prominent effects as mentioned above, insecticidal compositions within the present invention can be widely used for the prevention of epidemics by killing harmful insanitary insects, e.g. houseflies, mosquitoes and cockroaches, and for the control of common grain mites, Indian meal moths, rice weevils and like insects harmful to stored cereals. Furthermore, they are markedly effective for the control of insects harmful to agricultural crops, and horticultural and forest plants, examples of which insects are planthoppers, leafhoppers, stem borers, diamond-back moths, leaf rollers, aphids, spider mites and chestnut caterpillars, and also for the control of lice and ticks parasitic on animals and many other harmful insects. Compositions within the present invention are particularly low in toxicity to mammals and hence are excellent in that they can be freely applied to crops before harvest and to packaging materials for foods, and are safely usable for home horticulture and greenhouse cultivation.

Formulation procedures and insecticidal effects of compositions within the present invention are illustrated in more detail below with reference to Formulation Examples and Test Examples, in which all parts are by weight.

#### Formulation Example 1.

A mixture comprising 0.06 part of the ( $\pm$ )-cis, trans isomer of the compound (1) and 0.04 part of the ( $\pm$ )-trans isomer of the compound (3) was dissolved in deodorized kerosene to make the total amount 100 parts, whereby an oil preparation was obtained.

#### Formulation Example 2.

To a mixture comprising 0.04 part of the (+)-cis, trans isomer of the compound (1) and 0.01 part of the ( $\pm$ )-trans isomer of the compound (3) was added 0.25 part of piperonyl butoxide and the resulting mixture was

\*1: As previously defined.

0.15%

compound (3)

then dissolved in deodorized kerosene to make the total amount 100 parts, whereby an oil preparation was obtained.

#### Formulation Example 3.

5 A mixture comprising 4 parts of the ( $\pm$ )-cis, trans isomer of the compound (1) and 16 parts of the ( $\pm$ )-cis, trans isomer of the compound (3) was well stirred, together with 15 parts of Sorpol SM-200 (registered trademark for a surface active agent consisting of a mixture of an alkylphenol anion and a dodecylbenzenesulphonic acid anion and manufactured by Toho Chemical Co.) and 65 parts of xylene, whereby an emulsifiable concentrate was obtained.

#### Formulation Example 4.

20 A mixture comprising 0.2 part of the ( $\pm$ )-cis, trans isomer of the compound (1), 0.1 part of the (+)-trans isomer of the compound (3), 7 parts of xylene and 7.7 parts of deodorized kerosene was poured in an aerosol container. After attaching a valve portion to the container, 85 parts of a propellant (liquefied petroleum gas) was charged under pressure through the valve portion into the container to obtain an aerosol preparation.

#### Formulation Example 5.

30 A mixture comprising 0.2 part of the (+)-trans isomer of the compound (1), 0.1 part of the ( $\pm$ )-trans isomer of the compound (3), 13.7 parts of deodorized kerosene and 1 part of an emulsifier Atmos 300 (registered trademark for a monoglyceride surface active agent manufactured by Atlas Chemical Co.) was emulsified by addition of 50 parts of pure water. The resulting emulsion was charged, together with a 3:1 mixture of deodorized butane and deodorized propane, into an aerosol container to obtain a water-based aerosol preparation.

#### Formulation Example 6.

45 A mixture comprising 0.1 g of the (+)-cis, trans isomer of the compound (1), 0.3 g of the ( $\pm$ )-trans isomer of the compound (3) and 0.4 g of BHT was dissolved in 20 ml. of methanol, and then uniformly mixed with stirring with 99.2 g of a mosquito coil carrier (a 3:5:1 mixture of Tabu powder, pyrethrum marc and wood flour). The resulting mixture, after evaporation of methanol, was well kneaded with 150 ml. of water, and then shaped and dried to obtain a mosquito coil.

#### Formulation Example 7.

55 A mixture comprising 10 parts of the ( $\pm$ )-cis, trans isomer of the compound (1), 20 parts of the ( $\pm$ )-cis, trans isomer of the compound (3) and 5 parts of Sorpol SM-200 (as mentioned previously) was well stirred in a mortar together with 65 parts of 300-mesh talc to obtain a wettable powder.

#### Formulation Example 8.

A mixture comprising 2 parts of the (+)-trans isomer of the compound (1), 1 part of the ( $\pm$ )-trans isomer of the compound (3), and 10 parts of piperonyl butoxide was dissolved in 20 parts of acetone, and well stirred in a mortar together with 87 parts of diatomaceous earth capable of passing through a mesh having 300 holes per inch. Thereafter, acetone was removed by evaporation to obtain a dust preparation.

#### Formulation Example 9.

75 Two mixtures each comprising 2 parts of the ( $\pm$ )-cis, trans isomer of the compound (1) respectively with 2 parts of the ( $\pm$ )-trans and 2 parts of the ( $\pm$ )-cis, trans isomer of the compound (3) were each well stirred in respective mortars together with 5 parts of Toyolignin CT (registered trademark for a sodium ligninsulphonate dispersing agent manufactured by Toyo Spinning Co.) and 91 parts of GSM Clay (registered trademark of Zieklite Kogyo Co.). The resulting mixtures were each kneaded with 10% by weight based on the weight of the mixture of water, granulated by means of a granulator and then air-dried to obtain two fine granule preparations of the respective compound mixtures.

#### Formulation Example 10.

90 A mixture comprising 0.06 parts of the (+)-lon-(+)-cis, trans isomer of the compound (2) and 0.04 part of the ( $\pm$ )-trans isomer of the compound (3) was dissolved in deodorized kerosene to make the total amount 100 parts, whereby an oil preparation was obtained.

#### Formulation Example 11.

100 To a mixture comprising 0.04 part of the (+)-lon-(+)-trans isomer of the compound (2) and 0.01 part of the ( $\pm$ )-cis, trans isomer of the compound (3) was added 0.25 part of piperonyl butoxide and the resulting mixture was then dissolved in deodorized kerosene to make the total amount 100 parts, whereby an oil preparation was obtained.

#### Formulation Example 12.

110 To a mixture comprising 4 parts of the ( $\pm$ )-lon-( $\pm$ )-cis, trans isomer of the compound (2) and 16 parts of the ( $\pm$ )-cis, trans isomer of the compound (3) was added 15 parts of Sorpol SM-200 and 65 parts of xylene, and the resulting mixture was well stirred to obtain an emulsifiable concentrate.

#### Formulation Example 13.

115 A mixture comprising 0.2 part of the ( $\pm$ )-lon-(+)-cis, trans isomer of the compound (2), 0.1 part of the (+)-trans isomer of the compound (3), 7 parts of xylene and 7.7 parts of deodorized kerosene was poured into an aerosol container. After attaching a valve

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portion to the container, 85 parts of a propellant (liquified petroleum gas) was charged under pressure through the valve portion into the container to obtain an aerosol preparation.

Formulation Example 14.

A mixture comprising 0.2 part of the (+)-lon-(+)-trans isomer of the compound (2), 0.1 part of the (±)-cis, trans isomer of the compound (3), 13.7 parts of deodorized kerosene and 1 part of an emulsifier Atmos 300 (same as mentioned previously) was emulsified by addition of 50 parts of pure water. The resulting emulsion was charged, together with a 3:1 mixture of deodorized butane and deodorized propane, into an aerosol container to obtain a water-based aerosol preparation.

Formulation Example 15.

A mixture comprising 0.1 g of the (±)-lon-(±)-cis, trans isomer of the compound (2), 0.3 g of the (+)-cis, trans isomer of the compound (3) and 0.4 g of BHT was dissolved in 20 ml of methanol, and then uniformly mixed with stirring with 99.2 g of a mosquito coil carrier (a 3:5:1 mixture of Tabu powder, pyrethrum marc and wood flour). The resulting mixture, after evaporation of methanol, was well kneaded with 150 ml of water, and then shaped and dried to obtain a mosquito coil.

Formulation Example 16.

To each of two mixtures each comprising 0.02 g of the (±)-lon-(+)-trans isomer of the compound (2) respectively with 0.05 g of the (±)-cis, trans isomer and 0.03 g of (+)-trans isomer of the compound (3) was added 0.05 g of BHT and 0.1 g of piperonyl butoxide. The resulting mixture was dissolved in a suitable amount of chloroform, and uniformly adsorbed onto respective filter papers each of 3.5 cm x 1.5 cm in area and 0.3 cm in thickness to obtain fibrous fumigant compositions of the respective compound mixtures to be used by heating on an electrically heated plate.

As an alternative to the filter paper, there may be used any fibrous carriers, e.g. pulp or asbestos plates, which are equivalent in effectiveness to the filter paper, to obtain various fumigant compositions of this type.

Formulation Example 17.

A mixture comprising 10 parts of the (+)-lon-(+)-cis, trans isomer of the compound (2), 20 parts of the (±)-cis, trans isomer of the compound (3) and 5 parts of Sorpol SM-200 (as mentioned previously) was well stirred in a mortar together with 65 parts of talc capable of passing through a mesh having 300 holes per inch to obtain a wettable powder.

Formulation Example 18.

A mixture comprising 2 parts of the (±)-lon-(+)-trans isomer of the compound (2), 1 part of the (±)-trans isomer of the compound (3) and 10 parts of piperonyl butoxide was dissolved in 20 parts of acetone, and well stirred in a mortar together with 87 parts of 300-mesh diatomaceous earth. Thereafter, the acetone was removed by evaporation to obtain a dust preparation.

Formulation Example 19.

Two mixtures each comprising 2 parts of the (+)-lon-(+)-trans isomer of the compound (2) respectively with 2 parts of the (+)-trans and 2 parts of the (+)-cis, trans isomer of the compound (3) were each well stirred in a mortar together with 5 parts of Toyolignin CT (as mentioned previously) and 91 parts of GSM clay (as mentioned previously). The resulting mixtures were each kneaded with 10% by weight based on the weight of the mixture of water, granulated by means of a granulator and then air-dried to obtain two fine granule preparations of the respective compound mixtures.

Insecticidal effects of compositions within the present invention obtained in the above manner are as described in the following Test Examples:

Test Example 1.

Groups each of about 50 adult houseflies per group were introduced into respective glass chambers each of (70 cm)<sup>3</sup> and sprayed with 0.7 ml of one of each of the oil preparations obtained in Formulation Examples 1, 2 and 10 under a pressure of 1.5 kg/cm<sup>2</sup> using a glass atomizer, whereby more than 80% of the flies were knocked down within 10 minutes.

Test Example 2.

Using the Campbell's turn table method ["Soap & Sanitary Chemicals", Vol. 14, No. 6, page 119 (1938)], 5 ml of one of each of the oil preparations obtained in Formulation Examples 1, 2, 10 and 11 were sprayed, and groups each of about 100 adult houseflies were each exposed to one of the descending mists for 10 minutes. As a result, the death of more than 80% of the flies had occurred by the next day.

Test Example 3.

Each of the emulsifiable concentrates obtained in Formulation Examples 3 and 12 was diluted with water to form a 20,000-fold dilutions. 2 Litres of each dilution were poured into a respective polystyrene case of 23 cm in width, 30 cm in length and 6 cm in depth, and about 100 last-instar larvae of the Northern house mosquito were placed in each case. As a result, the death of more than 90% of the larvae had occurred by the next day.

## Test Example 4.

5 Rice plants, which had been grown for 45  
days after sowing, were grown in 1/50,000  
Wagner pots, and sprayed with 10 ml/pot of  
an aqueous 500-fold dilution of one of each  
of the emulsifiable concentrates obtained in  
Formulation Examples 3 and 12. Subse-  
quently, each pot was covered with a wire net,  
and about 30 adult green rice leafhoppers  
10 were introduced inside the net. As a result,  
the death of more than 90% of the leafhop-  
pers had occurred by the next day.

## Test Example 5.

15 Into each of a series of glass Petri dishes  
each of 14 cm in diameter were placed 10  
tobacco cutworm larvae at the third to fourth  
instar stage, and 1 ml. of an aqueous 200-fold  
dilution of one of each of the emulsifiable  
concentrates obtained in Formulation  
20 Examples 3 and 12 was sprayed onto the  
larvae using a spraying tower.

Thereafter, the larvae were transferred to  
another series of Petri dishes containing baits.  
As a result, the death of more than 90%  
25 of the cutworm larvae had occurred by the  
next day.

## Test Example 6.

30 Insecticidal effects on adult houseflies of  
the aerosol preparations obtained in Formulation  
Examples 4, 5, 13 and 14 were tested  
using the aerosol test method [described in  
"Soap & Chemical Specialties, Bluebook"  
(1965)] using a series of Peet Grady's cham-  
bers (6 ft)<sup>3</sup>. As a result, all the aerosol pre-  
parations knocked down more than 80% of  
35 the flies within 15 minutes after the spraying  
and more than 70% of the flies had died by  
the next day.

## Test Example 7.

40 Groups each of about 50 adult Northern  
house mosquitoes per group were each intro-  
duced into a respective glass chamber of  
(70 cm)<sup>3</sup>, and equipped with a small rotating  
electric fan of 13 cm in diameter. Subsequently  
45 0.1 g of one of each of the mosquito coils ob-  
tained in Formulation Examples 6 and 15 was  
ignited at one end and placed at the centre of  
the chamber bottom. As a result, all the mos-  
quito coils knocked down more than 90% of  
50 the mosquitoes and more than 80% thereof  
had died by the next day.

## Test Example 8.

55 A group of about 50 houseflies was intro-  
duced into a glass chamber of (70 cm)<sup>3</sup>, and  
equipped with a small rotating electric fan  
(13 cm in diameter). Subsequently, the fumi-  
gant composition obtained in Formulation  
Example 16 which is rendered effective on  
heating was placed on an electrically heated  
plate and fumigated in the chamber. As a  
60 result, more than 90% of the houseflies were  
knocked down within 20 minutes.

## Test Example 9.

Each of the dust preparations obtained in  
Formulation Examples 9 and 18 was uni-  
formly sprinkled in a proportion of 2 g/m<sup>2</sup>  
on to the bottom of a respective Petri dish of  
14 cm in diameter, and butter was then  
coated on the inner wall of each dish, except  
for the portion 1 cm from the bottom. Sub-  
sequently, a group of 10 adult German cock-  
roaches was introduced into each dish and con-  
tacted with one of the dust preparations for  
30 minutes, whereby more than 90% of the  
knocked down cockroaches were killed within  
3 days after the contact.

## Test Example 10.

Into a series of 14-litre polyethylene pails  
each containing 10 litres of water was placed  
1 g of one of each of the granule preparations  
obtained in Formulation Examples 9 and 19.  
After one day, groups each of about 100 last-  
instar larvae of the Northern house mosquito  
per group were immersed in the water in the  
respective pails, and the number of alive and  
dead of the larvae were observed with lapse  
of time. As a result, more than 90% of the  
larvae were killed within 24 hours.

## Test Example 11.

3 Grams of one of each of the oil prepara-  
tions obtained in Formulation Examples 2  
and 11 was fogged by means of an insect  
fogger (manufactured by Burgess Vibro-  
crafters, Inc., U.S.A.) into the same respec-  
tive Peet Grady's chambers as in Test  
Example 6 into each of which about 500  
houseflies had previously been introduced. As  
a result, more than 90% of the houseflies  
were knocked down within 30 minutes.

## Test Example 12.

Chinese cabbages were grown in a green  
house, and were artificially infested with cut-  
worms, cabbage worms and diamond-back  
moths. Thereafter, the green house (2 m in  
height) was divided into compartments of  
(30 m<sup>2</sup>) in area, and each compartment was  
fumigated using a thermofumigator  
(SEARCH) with 10 g of one of each of the  
wetttable powders obtained in Formulation  
Examples 7 and 17. As a result, substantially  
no increasing damage of the cabbages was  
observed.

## Test Example 13.

Mottled kidney bean plants (at the stage of  
2-leaves), which had been grown for 9 days  
after sowing in flower pots, were infested with  
10 to 15 female carmine mites per leaf, and  
then allowed to stand for a weak in a thermo-  
stat at 27°C, whereby the mites at various  
growth stages propagated in large numbers.  
At this stage, an aqueous 200-fold dilution  
of one of each of the emulsifiable concen-  
trates obtained in Formulation Examples 3

and 12 was sprayed onto respective plants in a proportion of 10 ml per pot, using a turntable. After 10 days, the plants were examined to find no substantial damage.

5 Test Example 14.

10 An aqueous 100-fold dilution of one of each of the wettable powders obtained in Formulation Examples 7 and 17 was applied in a proportion of 50 ml/m<sup>2</sup> onto the surface of a respective piece of plywood of 15 cm x 15 cm in area. Groups each of 20 adult Northern house mosquitoes per group were introduced into respective Petri dishes each of 9 cm in diameter. These dishes were placed upside down on a respective plywood surface treated with the said dilution to contact the mosquitoes with the treated surface and, after 60 minutes, the number of knocked down mosquitoes was counted.

15 In the above manner, the dilution applied to the plywood surface was examined to determine the knock-down effect on the day of application and thereafter once a week. As a result, the dilution showed a knock-down effect of more than 80% even after 4 weeks had elapsed from the day of application to the plywood surface, and thus was excellent in its residual effect.

WHAT WE CLAIM IS:—

30 1. An insecticidal composition containing an inert carrier and, as active ingredient, a mixture consisting of N - (3,4,5,6 - tetrahydrophthalimido) - methyl chrysanthemate [hereinafter referred to as the compound (1)] or 2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl chrysanthemate [hereinafter referred to as the compound (2)] and 3-phenoxybenzyl - 2',2' - dimethyl - 3' - (2'',2'' - dichlorovinyl) cyclopropanecarboxylate [hereinafter referred to as the compound (3)].

40 2. An insecticidal composition according to Claim 1, which contains from 0.05 to 90% inclusive by weight of the active ingredient.

3. An insecticidal composition according to

Claim 1 or Claim 2, wherein the mixing ratio of the compound (1) or (2) to the compound (3) is within a range of from 1:9 to 9:1 inclusive by weight. 45

4. An insecticidal composition according to Claim 1, Claim 2 or Claim 3, wherein the mixture is one consisting of the compound (1) and the compound (3). 50

5. An insecticidal composition according to Claim 1, Claim 2 or Claim 3, wherein the mixture is one consisting of the compound (2) and the compound (3). 55

6. An insecticidal composition according to Claim 5, wherein the compound (2) is (±)-2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl (+) - trans - chrysanthemate. 60

7. An insecticidal composition according to Claim 5, wherein the compound (2) is (+)-2 - allyl - 3 - methyl - cyclopent - 2 - ene - 1 - one - 4 - yl (+) - trans - chrysanthemate. 65

8. An insecticidal composition according to any one of the preceding Claims, wherein the compound (3) is 3-phenoxybenzyl-(±)-cis, trans - (2',2' - dimethyl - 3' - (2'',2'' - dichlorovinyl) cyclopropanecarboxylate. 70

9. An insecticidal composition according to any one of the preceding Claims, wherein the compound (3) is 3-phenoxybenzyl-(+)-trans - 2',2' - dimethyl - 3' - (2'',2'' - dichlorovinyl) cyclopropanecarboxylate. 75

10. A method of knocking down or killing insects, which comprises contacting the insects with an insecticidal composition according to Claim 1. 80

11. Insecticidal compositions according to any one of claims 1 to 9 substantially as herein described and exemplified. 85

12. Methods of knocking down or killing insects according to claim 10 substantially as herein described.

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