

## Pest-combating agents, their preparation and use

The present invention relates to new synergistic mixtures of the known active compounds 1R-(-)-[(pentafluorophenyl)-methyl]-3S-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate and O,O-dimethyl O-2,2-dichlorovinyl phosphate (dichlorvos) and, if appropriate, of O-isopropoxyphenyl N-methylcarbamate (propoxur), formulations (compositions) containing these active compound combinations, their preparation and use for combating arthropods.

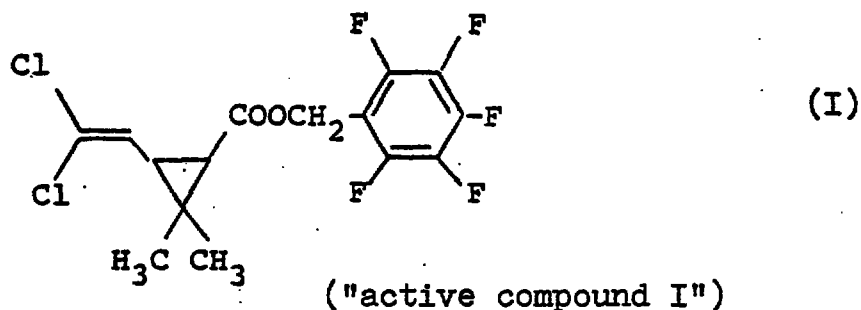
10        It is already known that propoxur and dichlorvos have a good action against insects and arachnidae. These active compounds have therefore been employed with great success for many years for combating pests, particularly for combating domestic vermin. However, 15 owing to the emergence of resistance, they suffer, like all insecticides hitherto which are in practical use, from certain losses in effect during the course of time, and these losses can, in certain cases, limit their suitability for use. The consequence of this is that, 20 in order to combat resistant pests, the required use concentrations and use quantities have constantly to be increased in order still to obtain a satisfactory action, until, finally, the limit is reached at which the use is no longer meaningful or possible, especially for economic 25 and application-technological reasons. The formation of resistant insect populations is particularly problematic in that their resistance is not only directed against a particular insecticide, but includes, as a rule, all active compounds of the same active compound 30 class, or even of several active compound classes which are similar in their action.

The solution of the problem of developing suitable agents for combating resistant pests is therefore of particularly great importance.

- 2 -

It has now been found that mixtures of the known active compounds

- I. 1R-(-)-[(pentafluorophenyl)-methyl]-3S-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate of the formula I



- II. O,O-dimethyl O-(2,2-dichlorovinyl) phosphate (common name: dichlorvos) of the formula II



("active compound II")

- 10 and, if appropriate,

- III 2-isopropoxy-phenyl N-methylcarbamate (common name: propoxur) of the formula III



("active compound III")

- 15 have a particularly powerful action against arthropods, particularly against insects and arachnidae.

The active compounds II and III are active compounds of known commercial products, and the active compound I is known from German Offenlegungsschrift (German Published Specification) 2,658,074.

- 20 The activity of the active compound combination,

- 3 -

according to the invention, of the two active compounds I and II, or of the three active compounds I, II and III, is surprisingly substantially greater than the sum of the activities of the individual compounds. A

5 genuine synergistic effect is thus present in the case of the combinations according to the invention.

The present inventions thus relate to mixtures of the two active compounds I and II, or of the three active compounds I, II and III, formulations (pest-  
10 combating agents) containing these mixtures, their preparation and use for combating arthropods, particularly insects and arachnidae, very particularly preferably insects.

The relative proportions of the active compounds  
15 can vary within relatively great ranges in the active compound mixtures or pest-combating agents according to the invention. The proportions (parts by weight) of the two components I and II are preferably between 1 : 100 and 1 : 1, particularly between 1 : 100 and  
20 1 : 10, and those of the three components I, II and III are between 1 : 100 : 100 and 1 : 1 : 1, particularly between 1 : 50 : 50 and 1 : 10 : 10. In these mixtures, the relative proportions of the components II and III can also vary within the limits given. Of course,  
25 these proportions do not have to correspond to integers.

Particularly preferred active compound mixtures or pest-combating agents are those in which the proportions (parts by weight) of the active compounds I and II are about 1 : 10, about 1 : 25 or about 1:50, and those  
30 of the active compounds I, II and III are about 1:10:25, about 1:25:25, about 1:25:50 or about 1:50:100.

The pest-combating agents according to the invention have an excellent knock-down action and fatal action against the most diverse destructive insects and arach-  
35 nidae, particularly insects. In this context, the rapid knock-down action is of great importance

- 4 -

particularly in combating domestic vermin, since the user lays particular value on a rapid elimination of the annoyance, especially for reasons of hygiene.

The new pest-combating agents are much more active  
5 against the pests which are resistant to carbamates, phosphoric (phosphonic) acid esters and pyrethroids, and can therefore be employed in much smaller quantities or concentrations, and with better success, than pest-combating agents which only contain 1R-(-)-  
10 [(pentafluorophenyl)-methyl]-3S-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate or dichlorvos or propoxur.

The abovementioned pests include, for example, the following pests:

15 From the order of the Thysanura, for example *Lepisma saccharina*. From the order of the Orthoptera, for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica* and *Aceta domesticus*. From the order of the Dermaptera, for  
20 example, *Forficula auricularia*. From the order of the Isoptera, for example, *Reticulitermes* spp.. From the order of the Heteroptera, for example, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma* spp. From the order of the Lepidoptera, for example, *Ephestia kuehniella*  
25 and *Galleria mellonella*. From the order of the Coleoptera, for example, *Anobium punctatum*, *Rhizopertha dominica*, *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Oryzaephilus surinamensis*, *Sitophilus* spp., *Dermestes* spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp.,  
30 *Lyctus* spp., *Ptinus* spp., *Niptus hololeucus*, *Gibbium psylloides*, *Tribolium* spp. and *Tenebrio molitor*. From the order of the Hymenoptera, for example, *Lasius* spp., *Monomorium pharaonis* and *Vespa* spp. From the order of the Diptera, for example, *Aedes* spp., *Anopheles* spp.,  
35 *Culex* spp., *Drosophila melanogaster*, *Musca* spp., *Fannia* spp., *Calliphora erythrocephala*, *Lucilia* spp., *Chrysomyia*

20

- 5 -

spp., Stomoxys spp. and Tabanus spp.. From the order of the Siphonaptera, for example, Xenopsylla cheopis and Ceratophyllus spp.. From the order of the Arachnida, for example, Scorpio maurus and Latrodectus mactans. From the order of the Acarina, for example, Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Boophilus spp., Rhicephalus spp., Amblyomma spp., Hyalomma spp. and Ixodes spp..

The active compound combinations can be converted to the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, pastes, soluble powders, aerosols, suspension/emulsion concentrates, natural and synthetic materials impregnated with active compound, very fine capsules in polymeric substances, and formulations used with burning equipment, such as fumigating cartridges, fumigating cans, fumigating coils and the like, as well as ULV cold mist and hot mist formulations.

These formulations are produced in known manner, for example by mixing the active compounds with extenders and formulation auxiliaries, that is, liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents.

In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents. As liquid solvents, there are suitable in the main: aromatics, such as xylene, toluene or alkyl naphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or ethylene glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone,

- 6 -

methy1 isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethylsulphoxide, as well as water; by liquefied gaseous extenders or carriers are meant liquids which are gaseous at normal temperature and under normal pressure, for example aerosol propellants, such as halogenated hydrocarbons as well as butane and propane as well as nitrogen, dinitrogen oxide and carbon dioxide; as solid carriers there are suitable: ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly dispersed silicic acid, alumina and silicates; as emulsifying agents there are suitable: non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, alkyl-aryl sulphonates as well as albumin hydrolysis products; as dispersing agents there are suitable: for example, lignin, sulphite waste liquors and methyl-cellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulations.

For use in baits, the formulations can contain the customary lures and baits, for example pheromones, attractive colorants, carbohydrates and proteins.

Aerosols, oil sprays and emulsion concentrates are particularly preferred formulations.

The formulations contain, in general, between 0.5 and 100% by weight of the active compound combinations, preferably between 0.5 and 60%.

The active compound combinations according to the invention are used in the form of their commercially available formulations and/or in the use forms prepared

- 7 -

from these formulations.

The active compound content of the use forms prepared from the commercially available formulations can vary within wide ranges. The active compound concentration of the use form can be from 0.01 to 100% by weight of active compounds, preferably between 0.1 and 10% by weight.

The compounds are employed in a customary manner appropriate for the use forms.

Because of their particular properties, the active compound mixtures according to the invention, or their formulations, can be employed in a wide range for combating arthropods. Preferred use areas are commercial and private hygiene (for example schools, hospitals, foodstuff-processing factories and households), commercial and private protection of stored products (for example foodstuff stores) and use in agriculture and animal husbandry (for example combating stable flies).

The following examples are intended to illustrate the preparation of the pest-combating agents according to the invention.

Formulation Examples:

|    |                                                                 |                 |
|----|-----------------------------------------------------------------|-----------------|
| 1) | Spray formulation                                               | Parts by weight |
|    | Active compound I                                               | 0.01            |
| 25 | Active compound II                                              | 1.0             |
|    | Methylene chloride                                              | 5.0             |
|    | Deodorised kerosene/mixture of saturated aliphatic hydrocarbons | 10.0            |
| 30 | Perfume oil                                                     | 0.01            |
|    | Propellant: propane/butane (15:85)                              | 83.98           |

- 8 -

|    |                                       |                 |
|----|---------------------------------------|-----------------|
| 2) | Spray formulation                     | Parts by weight |
|    | Active compound I                     | 0.04            |
|    | Active compound II                    | 1.0             |
|    | Methylene chloride                    | 5.0             |
| 5  | Deodorised kerosene                   | 10.0            |
|    | Perfume oil                           | 0.01            |
|    | Propellant: propane/butane<br>(15:85) | 83.95           |
| 3) | Spray formulation                     | Parts by weight |
| 10 | Active compound I                     | 0.04            |
|    | Active compound II                    | 1.0             |
|    | Active compound III                   | 2.0             |
|    | Methylene chloride                    | 25.0            |
|    | Deodorised kerosene                   | 12.43           |
| 15 | Perfume oil                           | 0.03            |
|    | Propellant: propane/butane<br>(15:85) | 59.50           |
| 4) | Oil spray formulation                 | Parts by weight |
|    | Active compound I                     | 0.08            |
| 20 | Active compound II                    | 0.5             |
|    | Isopropanol                           | 10.0            |
|    | Petroleum                             | 89.42           |
| 5) | Oil spray formulation                 | Parts by weight |
|    | Active compound I                     | 0.02            |
| 25 | Active compound II                    | 1.0             |
|    | Isopropanol                           | 10.0            |
|    | Petroleum                             | 88.98           |
| 6) | Oil spray formulation                 | Parts by weight |
|    | Active compound I                     | 0.04            |
| 30 | Active compound II                    | 1.0             |
|    | Active compound III                   | 1.0             |
|    | Isopropanol                           | 10.0            |
|    | Petroleum                             | 87.96           |

The following examples are intended to illustrate the activity of the active compound combinations according to the invention:

- 9 -

Biological Examples

Spray cans or oil sprays which contain either only active compound I or active compound II or active compound III, as well as spray cans or oil sprays which contain the active compounds I and II, or the active compounds I, II and III in combinations, are sprayed in rooms of 30 m<sup>3</sup> capacity. 3 wire cages, each containing 20 *Musca domestica* (♂♂, strain Hans) which are strongly resistant to carbamates, phosphoric (phosphonic) acid esters and pyrethroids, were previously hung in the rooms. After the application (by spraying) of 17 g of the formulations, in each case, per room, the rooms were closed and the action on the flies was continuously controlled for up to one hour. The test measured after how many minutes 50% (yields: K.D. 50 values) or 95% (yields: K.D. 95 values) of the test animals had been knocked down. The values determined are contained in the following table:

Table of test flies:

20 *Musca domestica* (strain Hans, ♂, multi-resistant)

|    | Active compounds | % (by weight) of active compounds in the formulation | Knock-down action in minutes after the application |         |
|----|------------------|------------------------------------------------------|----------------------------------------------------|---------|
|    |                  |                                                      | K.D. 50                                            | K.D. 95 |
| 25 | I                | 0.01 to 0.08                                         | none                                               | none    |
|    | II               | 0.5                                                  | none                                               | none    |
|    |                  | 1.0                                                  | 30                                                 | 55      |
|    | III              | 2.0                                                  | none                                               | none    |
| 30 | I                | 0.01                                                 |                                                    |         |
|    | +                | +                                                    | 28                                                 | 44      |
|    | II               | 1.0                                                  |                                                    |         |
|    | I                | 0.02                                                 |                                                    |         |
|    | +                | +                                                    | 21                                                 | 39      |
|    | II               | 1.0                                                  |                                                    |         |

- 10 -

## Continuation

Table of test flies:Musca domestica (strain Hans,  $\omega$ , multi-resistant)

| 5  | Active compounds | % (by weight) of active compounds in the formula-tions | Knock-down action in minutes after the application |         |
|----|------------------|--------------------------------------------------------|----------------------------------------------------|---------|
|    |                  |                                                        | K.D. 50                                            | K.D. 95 |
| 10 | I                | 0.04                                                   |                                                    |         |
|    | +                | +                                                      | 18                                                 | 34      |
|    | II               | 1.0                                                    |                                                    |         |
| 15 | I                | 0.03                                                   |                                                    |         |
|    | +                | +                                                      | 23                                                 | 51      |
|    | II               | 0.5                                                    |                                                    |         |
| 20 | I                | 0.08                                                   |                                                    |         |
|    | +                | +                                                      | 20                                                 | 40      |
|    | II               | 0.5                                                    |                                                    |         |
| 25 | I                | 0.02                                                   |                                                    |         |
|    | +                | +                                                      | 18                                                 | 33      |
|    | II               | 1.0                                                    |                                                    |         |
| 30 | +                |                                                        |                                                    |         |
|    | III              | 2.0                                                    |                                                    |         |
| 25 | I                | 0.03                                                   |                                                    |         |
|    | +                | +                                                      |                                                    |         |
|    | II               | 1.0                                                    | 16                                                 | 26      |
| 30 | +                |                                                        |                                                    |         |
|    | III              | 2.0                                                    |                                                    |         |
| 30 | I                | 0.04                                                   |                                                    |         |
|    | +                | +                                                      | 14                                                 | 21      |
|    | II               | 1.0                                                    |                                                    |         |
| 30 | +                |                                                        |                                                    |         |
|    | III              | 2.0                                                    |                                                    |         |

"None" denotes that a K.D. 50 or K.D. 95 was not achieved during the course of 1 hour.

Patent Claims

1. Active compound mixtures comprising  
I) 1R-(-)-[(pentafluorophenyl)-methyl]-3S-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate ("active compound I") and  
II) O,O-dimethyl O-(2,2-dichlorovinyl) phosphate ("active compound II") and, if appropriate,  
III) 2-isopropoxy-phenyl N-methylcarbamate ("active compound III").
2. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I and II are between 1 : 100 and 1 : 1.
3. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I and II are between 1:100 and 1:10.
4. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I, II and III are between 1:100:100 and 1:1:1.
5. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I, II and III are between 1:100:100 and 1:10:10.
6. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I and II are about 1:10, about 1:25 or about 1:50.
7. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I, II and III are about 1:10:25, about 1:25:25, about 1:25:50 or about 1:50:100.
8. Use of active compound mixtures according to Claims 1 to 7 for combating arthropods.
9. Pest-combating agents characterised in that they contain an active compound mixture according to Claims 1 to 7.



### Ansprüche (as printed)

1. Wirkstoffmischungen bestehend aus
  - I) [(Pentafluorphenyl)-methyl]-(-)-1R, 3S-3-(2,2-dichlorethenyl)-2,2-dimethylcyclopropanecarboxylat (« Wirkstoff I ») und
  - II) 0,0-Dimethyl-O-(2,2-dichlorovinyl)phosphat (« Wirkstoff II ») und gegebenenfalls
  - III) 2-isopropoxy-phenyl-N-methylcarbamate (« Wirkstoff III »).
2. Wirkstoffmischungen gemäß Anspruch 1, in welchen die Mengenverhältnisse (Gewichtsteile) der Wirkstoffe I und II zwischen 1 : 100 und 1 : 1 liegen.
3. Wirkstoffmischungen gemäß Anspruch 1, in welchen die Mengenverhältnisse (Gewichtsteile) der Wirkstoffe I und II zwischen 1 : 100 und 1 : 10 liegen.
4. Wirkstoffmischungen gemäß Anspruch 1, in welchen die Mengenverhältnisse (Gewichtsteile) der Wirkstoffe I, II und III zwischen 1 : 100 : 100 und 1 : 1 : 1 liegen.
5. Wirkstoffmischungen gemäß Anspruch 1, in welchen die Mengenverhältnisse (Gewichtsteile) der Wirkstoffe I, II und III zwischen 1 : 100 : 100 und 1 : 10 : 10 liegen.
6. Wirkstoffmischungen gemäß Anspruch 1, in welchen die Mengenverhältnisse (Gewichtsteile) der Wirkstoffe I und II bei etwa 1 : 10, etwa 1 : 25 oder etwa 1 : 50 liegen.
7. Wirkstoffmischungen gemäß Anspruch 1, in welchen die Mengenverhältnisse (Gewichtsteile) der Wirkstoffe I, II und III bei etwa 1 : 10 : 25, etwa 1 : 25 : 25, etwa 1 : 25 : 50 oder etwa 1 : 50 : 100 liegen.
8. Verwendung von Wirkstoffmischungen gemäß den Ansprüchen 1 bis 7 zur Bekämpfung von Arthropoden.
9. Schädlingsbekämpfungsmittel, gekennzeichnet durch den Gehalt an einer Wirkstoffmischung gemäß den Ansprüchen 1 bis 7.

### Claims (as printed)

1. Active compound mixtures comprising
  - I) 1R-(-)-[(pentafluorophenyl)-methyl]-3S-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (« active compound I ») and
  - II) 0,0-dimethyl O-(2,2-dichlorovinyl) phosphate (« active compound II ») and, if appropriate,
  - III) 2-isopropoxy-phenyl N-methylcarbamate (« active compound III »).
2. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I and II are between 1 : 100 and 1 : 1.
3. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I and II are between 1 : 100 and 1 : 10.
4. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I, II and III are between 1 : 100 : 100 and 1 : 1 : 1.
5. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I, II and III are between 1 : 100 : 100 and 1 : 10 : 10.
6. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I and II are about 1 : 10, about 1 : 25 or about 1 : 50.
7. Active compound mixtures according to Claim 1, wherein the proportions (parts by weight) of the active compounds I, II and III are about 1 : 10 : 25, about 1 : 25 : 25, about 1 : 25 : 50 or about 1 : 50 : 100.
8. Use of active compound mixtures according to Claims 1 to 7 for combating arthropods.
9. Pest-combating agents characterised in that they contain an active compound mixture according to Claims 1 to 7.

**Revendications (as printed)**

1. Mélanges de substances actives constitués par
  - I) le (-)-1R,3S-3-(2,2-dichloréthényl)-2,2-diméthylcyclopropanecarboxylate de [[pentafluorophényl)-méthyle] (« substance active I ») et
  - II) le phosphate de 0,0-diméthyle et de 0-(2,2-dichlorovinyle) (« substance active II ») et, le cas échéant
  - III) le N-méthylcarbamate de 2-isopropoxyphénylie (« substance active III »).
2. Mélanges de substances actives suivant la revendication 1, dans lesquels les rapports des quantités (parties en poids) des substances actives I et II se situent entre 1 : 100 et 1 : 1.
3. Mélanges de substances actives suivant la revendication 1, dans lesquels les rapports des quantités (parties en poids) des substances actives I et II se situent entre 1 : 100 et 1 : 10.
4. Mélanges de substances actives suivant la revendication 1, dans lesquels les proportions des quantités (parties en poids) des substances actives I, II et III se situent entre 1 : 100 : 100 et 1 : 1 : 1.
5. Mélanges de substances actives suivant la revendication 1, dans lesquels les proportions des quantités (parties en poids) des substances actives I, II et III se situent entre 1 : 100 : 100 et 1 : 10 : 10.
6. Mélanges de substances actives suivant la revendication 1, dans lesquels les rapports des quantités (parties en poids) des substances actives I et II ont des valeurs d'environ 1 : 10, d'environ 1 : 25 ou d'environ 1 : 50.
7. Mélanges de substances actives suivant la revendication 1, dans lesquels les proportions des quantités (parties en poids) des substances actives I, II et III ont des valeurs d'environ 1 : 10 : 25, d'environ 1 : 25 : 25, d'environ 1 : 25 : 50 ou d'environ 1 : 50 : 100.
8. Utilisation de mélanges de substances actives suivant les revendications 1 à 7 pour combattre des arthropodes.
9. Compositions pesticides, caractérisées par une teneur en un mélange de substances actives suivant les revendications 1 à 7.