

# PATENT SPECIFICATION

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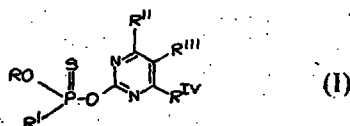
## (54) PYRIMIDINYLTHIONOPHOSPHONIC ACID ESTERS, PROCESS FOR THEIR PREPARATION AND THEIR USE AS INSECTICIDES, ACARICIDES AND NEMATOCIDES

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany of Leverkusen, Germany, 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 certain new pyrimidinylthionophosphonic acid esters, to a process for their preparation and to their use as insecticides, acaricides and nematocides.

It is already known that pyrimidinylthionophosphoric acid esters, for example, O,O-dimethyl- and O,O-diethyl-O-pyrimidin(2)yl-thionophosphoric acid ester or O,O-diethyl-O-[2-isopropyl-4-methyl-pyrimidin(6)yl]-thionophosphoric acid ester, have insecticidal and acaricidal properties (compare U.S. Patent Specification 3,741,968 and German Patent Specification 947,208).

The present invention provides pyrimidinylthionophosphonic acid esters of the general formula



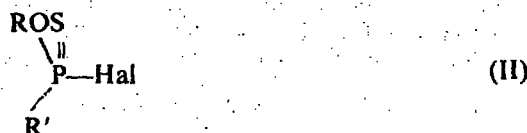
in which

R represents alkyl with 1 to 6 carbon atoms,  
 R' represents alkyl with 1 to 6 carbon atoms or phenyl,  
 R'' and R<sup>IV</sup>, which can be the same or different, represent alkyl with 1 to 4 carbon atoms or hydrogen, and  
 R''' represents halogen or hydrogen.

Preferably, R represents straight-chain or branched alkyl with 1 to 4 carbon atoms, R' represents straight-chain or branched alkyl with 1 to 4 carbon atoms or phenyl, R'' and R<sup>IV</sup> represent hydrogen, methyl or ethyl, and R''' represents hydrogen, chlorine or bromine.

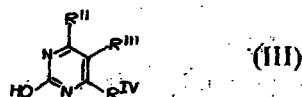
These compounds have been found to possess strong insecticidal, acaricidal and nematocidal properties.

The invention also provides a process for the production of a pyrimidinylthionophosphonic acid ester of the formula (I) in which an O-alkylthionophosphonic acid ester halide of the general formula



in which

R and R' have the above-mentioned meanings and Hal represents halogen, preferably chlorine, is reacted with a 2-hydroxypyrimidine derivative of the general formula



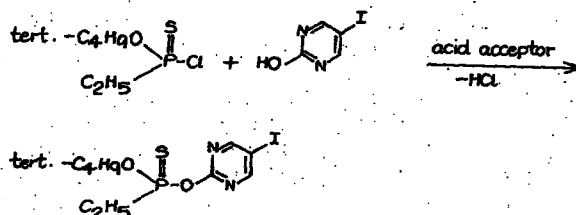
in which

R'', R''' and R'''' have the above-mentioned meanings, in the form of the free base or the hydrochloride or an alkali metal salt, alkaline earth metal salt or ammonium salt.

The reaction may of course be carried out in the presence of an acid acceptor when the 2-hydroxypyrimidine derivative is one which makes this appropriate.

Surprisingly, the pyrimidinylthionophosphonic acid esters according to the invention have a better insecticidal (including soil-insecticidal), acaricidal and nematocidal action than the previously known compounds of analogous structure and of the same type of action. The new products are not only active against foliage insects and soil insects, mites and nematodes, but also against hygiene pests and pests of stored products. Accordingly, they represent a genuine enrichment of the art.

If, for example, O-tert.-butyl-thionoethanephosphonic acid ester chloride and 2-hydroxy-5-iodo-pyrimidine are used as starting materials, the course of the reaction can be represented by the following formula scheme:



The formulae (II) and (III) provide an unambiguous definition of the starting materials to be used.

The O-alkylthionophosphonic acid ester halides (II) to be used as starting materials are known from the literature and can be prepared in accordance with generally customary processes.

The following may be mentioned individually as examples of these halides: O-methyl-, O-ethyl-, O-n-propyl-, O-isopropyl-, O-n-butyl-, O-sec.-butyl-, O-iso-butyl- and O-tert.-butyl-methane-, -ethane-, -n-propane-, -iso-propane-, -n-butane-, -iso-butane-, -sec.-butane-, -tert.-butane- and -phenyl-thionophosphonic acid ester chloride.

The 2-hydroxypyrimidine derivatives (III), some of which are new, can be prepared in accordance with processes known from the literature, for example by reacting 1,1,3,3-tetraalkoxypropane and urea, in alcoholic solution, with hydrogen chloride (compare U.S. Patent Specification 3,741,968); the halogenated derivatives can be prepared therefrom by reaction with halogenating agents, for example bromine.

The following may be mentioned individually as examples of 2-hydroxypyrimidine derivatives (III) for use in the process of the invention: 4,6-dimethyl-, 4,6-diethyl-, 4-methyl-, 4-ethyl-, 5-chloro- and 5-bromo-2-hydroxypyrimidine and 2-hydroxypyrimidine.

The reaction according to the invention is preferably carried out in the presence of a solvent (this term includes a mere diluent). Practically all inert organic solvents can be used for this purpose. These include, in particular, aliphatic and aromatic (optionally chlorinated) hydrocarbons, for example benzene, toluene, xylene, benzine, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene; ethers, for example diethyl ether, dibutyl ether and dioxan; ketones, for example acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; and nitriles, for example acetonitrile and propionitrile.

All customary acid-binding agents can be used as acid acceptors. Alkali metal carbonates and alkali metal alcoholates, such as sodium carbonate and potassium carbonate, sodium methylate and ethylate and potassium methylate and ethylate, have proved particularly suitable, as have aliphatic, aromatic or heterocyclic amines, for example triethylamine, trimethylamine, dimethylaniline, dimethylbenzylamine and pyridine.

The reaction temperature can be varied within a substantial range. In general, the reaction is carried out at 0° to 100°C, preferably at 40° to 55°C.

The reaction is in general allowed to take place under normal pressure. In carrying out the process according to the invention, the reactants are in general employed in equimolar ratios. The reaction is preferably carried out in the presence of one of the above-mentioned solvents or diluents (and, when appropriate, in the presence of an acid acceptor) at the temperatures indicated. After completion of the reaction, the mixture may be worked up in the usual manner, for example by adding an organic solvent to the reaction mixture and washing, drying and distilling the organic phase.

The new compounds are frequently obtained in the form of oils which in most cases cannot be distilled without decomposition but may be freed from the last volatile constituents by so-called "slight distillation", that is to say by prolonged heating under reduced pressure to moderately elevated temperatures, and they may be purified in this way. They are characterised by the refractive index. Some compounds are obtained in a crystalline form of sharp melting point.

As has already been mentioned, the pyrimidinylthionophosphonic acid esters according to the invention are distinguished by an excellent foliage-insecticidal and soil-insecticidal, acaricidal and nematocidal activity. They are active against plant pests, hygiene pests and pests of stored products. They have a good action both against sucking and against biting insects and mites.

For this reason, the compounds according to the invention can be employed successfully as pesticides in plant protection and in the hygiene field and the field of protection of stored products.

To the sucking insects there belong, in the main, aphids (*Aphididae*) such as the green peach aphid (*Myzus persicae*), the bean aphid (*Doralis fabae*), the bird cherry aphid (*Rhopalosiphum padi*), the pea aphid (*Macrosiphum pisi*) and the potato aphid (*Macrosiphum solanifolii*), the currant gall aphid (*Cryptomyzus korschelti*), the rosy apple aphid (*Sappaphis mali*), the mealy plum aphid (*Hyalopterus arundinis*), and the cherry black-fly (*Myzus cerasi*); in addition, scales and mealybugs (*Coccina*), for example the oleander scale (*Aspidiotus hederae*) and the soft scale (*Lecanium hesperidum*) as well as the grape mealybug (*Pseudococcus maritimus*); thrips (*Thysanoptera*), such as *Hercinothrips femoralis*, and bugs, for example the beet bug (*Piesma quadrata*), the red cotton bug (*Dysdercus intermedius*), the bed bug (*Cimex lectularius*), the assassin bug (*Rhodnius prolixus*) and Chagas' bug (*Triatoma infestans*) and, further, cicadas, such as *Euscelis bilobatus* and *Nephotettix bipunctatus*.

In the case of the biting insects, above all there should be mentioned butterfly caterpillars (*Lepidoptera*) such as the diamond-back moth (*Plutella maculipennis*), the gipsy moth (*Lymantria dispar*), the brown-tail moth (*Euproctis chrysorrhoea*) and tent caterpillar (*Malacosoma neustria*); further, the cabbage moth (*Mamestra brassicae*) and the cut-worm (*Agrotis segetum*), the large white butterfly (*Pieris brassicae*), the small winter moth (*Cheimatobia brumata*), the green oak tortrix moth (*Tortrix viridana*), the fall armyworm (*Laphygma frugiperda*) and cotton worm (*Prodenia litura*), the ermine moth (*Hyponomeuta padella*), the Mediterranean flour moth (*Ephestia kühniella*) and greater wax moth (*Galleria mellonella*).

Also to be classed with the biting insects are beetles (*Coleoptera*), for example the granary weevil (*Sitophilus granarius* = *Calandra granaria*), the Colorado beetle (*Leptinotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius* = *Acanthoscelides obtectus*), the leather beetle (*Dermestes frischii*), the khapra beetle (*Trogoderma granarium*), the flour beetle (*Tribolium castaneum*), the northern corn billbug (*Calandra* or *Sitophilus zeamais*), the drugstore beetle (*Stegobium paniceum*), the yellow mealworm (*Tenebrio molitor*) and the saw-toothed grain beetle (*Oryzaephilus surinamensis*), but also species living in the soil, for example wireworms (*Agriotes spec.*) and larvae of the cockchafer (*Melolontha melolontha*); cockroaches, such as the German cockroach (*Blattella germanica*), American cockroach (*Periplaneta americana*), Madeira cockroach (*Leucophaea* or *Rhyparobia maderae*), oriental

cockroach (*Blatta orientalis*), the giant cockroach (*Blaberus giganteus*) and the black giant cockroach (*Blaberus fuscus*) as well as *Henschoultedenia flexivitta*; further, *Orthoptera*, for example the house cricket (*Gryllus domesticus*); termites such as the eastern subterranean termite (*Reticulitermes flavipes*) and *Hymenoptera* such as ants, for example the garden ant (*Lasius niger*).

The *Diptera* comprise essentially the flies, such as the vinegar fly (*Drosophila melanogaster*), the Mediterranean fruit fly (*Ceratitidis capitata*), the house fly (*Musca domestica*), the little house fly (*Fannia canicularis*), the black blow fly (*Phormia regina*) and bluebottle fly (*Calliphora erythrocephala*) as well as the stable fly (*Stomoxys calcitrans*); further, gnats, for example mosquitoes such as the yellow fever mosquito (*Aedes aegypti*), the northern house mosquito (*Culex pipiens*) and the malaria mosquito (*Anopheles stephensi*).

With the mites (*Acari*) there are classed, in particular, the spider mites (*Tetranychidae*) such as the two-spotted spider mite (*Tetranychus urticae*) and the European red mite (*Paratetranychus pilosus* = *Panonychus ulmi*), gall mites, for example the blackcurrant gall mite (*Eriophyes ribis*) and tarsonemids, for example the broad mite (*Hemitarsonemus latus*) and the cyclamen mite (*Tarsonemus pallidus*); finally, ticks, such as the relapsing fever tick (*Ornithodoros moubata*).

The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid or liquefied gaseous diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents, and/or foam-forming 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 diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes, toluene, benzene or alkyl naphthalenes, chlorinated aromatic or 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 glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethyl formamide, dimethyl sulphoxide or acetonitrile, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperatures and pressures, e.g. aerosol propellants, such as halogenated hydrocarbons, e.g. Freon. "Freon" is a Registered Trade Mark.

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, or ground synthetic minerals, such as highly-dispersed silicic acid, alumina or silicates.

Preferred examples of emulsifying and foam-forming agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates and aryl sulphonates as well as albumin hydrolyzation products; and preferred examples of dispersing agents include lignin, sulphite waste liquors and methyl cellulose.

The active compounds according to the invention can be used as a mixture with other active compounds.

The formulations in general contain from 0.1 to 95 per cent by weight of active compound, preferably 0.5 to 90%.

The active compounds can be used as such, in the form of their formulations or the application forms prepared therefrom, such as ready-to-use solutions, emulsions, foams, suspensions, powders, pastes, soluble powders, dusting agents and granules. They may be applied in the customary manner, for example by squirting, spraying, atomising, dusting, scattering, fumigating, gassing, watering, dressing or encrusting.

The compositions may be diluted for actual application, and the active compound concentrations in the ready-to-use preparations can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably 0.01 to 1%, by weight.

The active compounds can also be used with good success in the ultra-low volume (ULV) method, where it is possible to apply formulations of up to 95% strength or even the 100% strength active compound by itself.

The invention therefore provides an insecticidal, acaricidal or nematocidal

composition containing as active ingredient a compound according to the invention in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The invention also provides a method of combating insect, acarid or nematode pests which comprises applying to the pests or a habitat thereof a compound according to the invention alone or in the form of a composition containing as active ingredient a compound according to the invention in admixture with a diluent or carrier.

The invention also provides crops protected from damage by insects, acarids or nematodes by being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to the invention was applied alone or in admixture with a diluent or carrier. It will be seen that the usual methods of providing a harvested crop may be improved by the present invention.

The compounds according to the invention, and the preparation and use of the compounds according to the invention, are illustrated by the following Examples.

In the use Examples A to J, the active compounds according to the invention were tested, in respect of their activity against a range of plant pests, in comparison to the known O,O-dimethyl- and O,O-diethyl-O-[pyrimidin(2)yl]-phosphoric acid ester and O,O-diethyl-O-[2-isopropyl-4-methylpyrimidin(6)yl]-thionophosphoric acid ester, which are designated (A), (B) and (C) respectively in these Examples. The new substances tested are identified, in these Examples, by the figure shown in each case in parentheses, which is that of the corresponding preparation Example.

#### Example A.

##### Critical concentration test/soil insects

Test insect: *Phorbia antiqua* grubs

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with the stated amount of solvent, the stated amount of emulsifier was added and the concentrate was diluted with water to the desired concentration.

The preparation of active compound was intimately mixed with the soil. The concentration of the active compound in the preparation was practically immaterial, the only decisive factor being the amount by weight of active compound per unit volume of soil, which is quoted in ppm (=mg/l). The soil was filled into pots and the pots were left to stand at room temperature.

After 24 hours the test animals were introduced into the treated soil and after a further 2 to 7 days the degree of effectiveness of the active compound was determined in % by counting the dead and live test insects. The degree of effectiveness was 100% if all test insects had been killed and was 0% if exactly as many test insects were still alive as in the case of the untreated control.

The active compounds, amounts used and results can be seen from the table which follows:

TABLE A

Soil insecticide test/*Phorbia antiqua* grubs in the soil

| Active compound | Degree of destruction in %<br>at an active compound<br>concentration of 2.5 ppm. |
|-----------------|----------------------------------------------------------------------------------|
| [B]             | 0                                                                                |
| [A]             | 0                                                                                |
| (4)             | 100                                                                              |
| (6)             | 100                                                                              |
| (1)             | 100                                                                              |
| (9)             | 100                                                                              |
| (10)            | 100                                                                              |
| (12)            | 100                                                                              |
| (13)            | 100                                                                              |
| (14)            | 100                                                                              |
| (15)            | 100                                                                              |
| (16)            | 100                                                                              |
| (18)            | 100                                                                              |

## Example B.

Critical concentration test/soil insects

Test insect: *Tenebrio molitor* larvae

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with the stated amount of solvent, the stated amount of emulsifier was added and the concentrate was diluted with water to the desired concentration.

The preparation of active compound was intimately mixed with the soil. The concentration of the active compound in the preparation was practically immaterial, the only decisive factor being the amount by weight of active compound per unit volume of soil, which is quoted in ppm (=mg/l). The soil was filled into pots and the pots were left to stand at room temperature.

After 24 hours the test animals were introduced into the treated soil and after a further 2 to 7 days the degree of effectiveness of the active compound was determined in % by counting the dead and live test insects. The degree of effectiveness was 100% if all test insects had been killed and was 0% if exactly as many test insects were still alive as in the case of the untreated control.

The active compounds, amounts used and results can be seen from the table which follows:

TABLE B

Soil insecticide test/*Tenebrio molitor* larvae in the soil

| Active compound | Degree of destruction in %<br>at an active compound<br>concentration of 10 ppm |
|-----------------|--------------------------------------------------------------------------------|
| [A]             | 0                                                                              |
| (4)             | 100                                                                            |
| (6)             | 100                                                                            |
| (1)             | 100                                                                            |
| (12)            | 100                                                                            |
| (13)            | 100                                                                            |
| (14)            | 100                                                                            |
| (15)            | 100                                                                            |
| (16)            | 100                                                                            |

## Example C.

Critical concentration test

Test nematode: *Meloidogyne incognita*

Solvent: 3 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with the stated amount of solvent, the stated amount of emulsifier was added and the concentrate was diluted with water to the desired concentration.

The preparation of active compound was intimately mixed with soil which was heavily infested with the test nematodes. The concentration of the active compound in the preparation was of practically no importance; only the amount of active compound per unit volume of soil, which is given in ppm, was decisive. The treated soil was filled into pots, lettuce was sown in and the pots were kept at a greenhouse temperature of 27°C.

After 4 weeks, the lettuce roots were examined for infestation with nematodes (root knots), and the degree of effectiveness of the active compound was determined as a percentage. The degree of effectiveness was 100% when infestation was completely avoided; it was 0% when the infestation was exactly the same as in the case of the control plants in untreated soil which had been infested in the same manner.

The active compounds, the amounts applied and the results can be seen from the following table C:

TABLE C

Nematocide test/*Meloidogyne incognita*

| Active compound | Degree of destruction in %<br>at an active compound<br>concentration of 10 ppm |
|-----------------|--------------------------------------------------------------------------------|
| [A]             | 0                                                                              |
| [C]             | 0                                                                              |
| (4)             | 100                                                                            |
| (6)             | 100                                                                            |
| (1)             | 100                                                                            |
| (10)            | 100                                                                            |
| (12)            | 100                                                                            |
| (14)            | 100                                                                            |
| (15)            | 100                                                                            |

## Example D.

*Drosophila* test

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier, and the concentrate was diluted with water to the desired concentration.

1 cm<sup>3</sup> of the preparation of the active compound was applied with a pipette to a filter paper disc of 7 cm diameter. The wet disc was placed over the orifice of a glass vessel containing 50 vinegar flies (*Drosophila melanogaster*) and covered with a glass plate.

After the specified periods of time, the destruction was determined in %. 100% means that all the flies were killed; 0% means that no flies were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following table D:

TABLE D

(Drosophila test)

| Active compound | Active compound<br>concentration<br>in % by weight | Degree of<br>destruction in %<br>after 1 day |
|-----------------|----------------------------------------------------|----------------------------------------------|
| [A]             | 0.001                                              | 100                                          |
|                 | 0.0001                                             | 0                                            |
| (5)             | 0.0001                                             | 100                                          |
| (10)            | 0.0001                                             | 100                                          |
| (11)            | 0.0001                                             | 100                                          |
| (14)            | 0.0001                                             | 100                                          |

## Example E.

*Doralis* test (Systemic action)

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate was diluted with water to the desired concentration.

Bean plants (*Vicia faba*) which had been heavily infested with the bean aphid (*Doralis fabae*) were watered with the preparation of the active compound so that the preparation penetrated into the soil without wetting the leaves of the bean plants. The active compound was taken up from the soil by the bean plants and thus passed to the infested leaves.

After the specified periods of time, the degree of destruction was determined as a percentage. 100% means that all the aphids were killed; 0% means that none of the aphids were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following table E:

TABLE E

(Doralis test/systemic action)

| Active compound | Active compound concentration in % by weight | Degree of destruction in % after 4 days |
|-----------------|----------------------------------------------|-----------------------------------------|
| [C]             | 0.1                                          | 100                                     |
|                 | 0.01                                         | 0                                       |
| (3)             | 0.01                                         | 100                                     |
| (4)             | 0.01                                         | 95                                      |
| (11)            | 0.01                                         | 100                                     |
| (16)            | 0.01                                         | 100                                     |
| (19)            | 0.01                                         | 100                                     |

## Example F.

*Tetranychus* test (resistant)

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Bean plants (*Phaseolus vulgaris*), which had a height of approximately 10—30 cm, were sprayed with the preparation of the active compound until dripping wet. These bean plants were heavily infested with the common or two-spotted spider mite (*Tetranychus urticae*) in all stages of development.

After the specified periods of time, the degree of destruction was determined as a percentage: 100% means that all the spider mites were killed; 0% means that none of the spider mites were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following table F:

TABLE F

(Tetranychus test)

| Active compound | Active compound concentration in % by weight | Degree of destruction in % after 2 days |
|-----------------|----------------------------------------------|-----------------------------------------|
| [C]             | 0.1                                          | 100                                     |
|                 | 0.01                                         | 0                                       |
| (10)            | 0.1                                          | 100                                     |
|                 | 0.01                                         | 80                                      |
| (14)            | 0.1                                          | 100                                     |
|                 | 0.01                                         | 99                                      |
| (15)            | 0.1                                          | 100                                     |
|                 | 0.01                                         | 100                                     |
| (18)            | 0.1                                          | 100                                     |
|                 | 0.01                                         | 99                                      |

## Example G.

Plutella test (long-term action after spraying)

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent and the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cabbage plants (*Brassica oleracea*) which were about 10—15 cm high were sprayed with the preparation of active compound until dripping wet.

After the specified periods of time, the plants were infested with caterpillars of the diamond-back moth (*Plutella maculipennis*). After 3 days, the destruction was determined as a percentage. 100% means that all the caterpillars had been killed; 0% means that none of the caterpillars had been killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from Table G which follows:

TABLE G

Long-term action after spraying with 0.05% by weight of active compound

(Plutella maculipennis on Brassica oleracea)

| Active compound | % destruction after |        |         |
|-----------------|---------------------|--------|---------|
|                 | 4 days              | 8 days | 11 days |
| [C]             | 50                  | 0      |         |
| (8)             | 100                 | 100    | 100     |
| (13)            | 100                 | 100    | 100     |

## Example H.

## Plutella test (long-term action after watering)

Solvent: 3 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent and the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cabbage plants (*Brassica oleracea*) were each watered with 50 ml of the preparation of active compound so that this preparation penetrated into the soil without wetting the leaves of the cabbage plants. The active compound was taken up by the cabbage plants from the soil and thus passed to the leaves.

After the specified periods of time, the plants were infested with caterpillars of the diamond-back moth (*Plutella maculipennis*). After 3 days, the destruction was determined as a percentage. 100% means that all the caterpillars had been killed. 0% means that none of the caterpillars had been killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from Table H which follows:

TABLE H

Long-term action after watering with  
0.025% by weight of active compound  
(*Plutella maculipennis* on *Brassica oleracea*)

| Active compound | % destruction after |        |         |         |
|-----------------|---------------------|--------|---------|---------|
|                 | 4 days              | 8 days | 11 days | 15 days |
| [C]             | 100                 | 90     | 0       |         |
| (3)             | 100                 | 100    | 100     | 100     |
| (4)             | 100                 | 100    | 100     | 100     |
| (5)             | 100                 | 100    | 100     | 100     |
| (1)             | 100                 | 100    | 100     | 100     |
| (9)             | 100                 | 100    | 100     | 90      |
| (10)            | 100                 | 100    | 100     | 100     |
| (11)            | 100                 | 100    | 100     | 100     |
| (12)            | 100                 | 100    | 100     | 100     |
| (14)            | 100                 | 100    | 100     | 100     |
| (15)            | 100                 | 100    | 100     | 100     |

Example J.  
LT<sub>100</sub> test for Diptera

Test animals: *Musca domestica*

Solvent: Acetone

2 parts by weight of active compound were dissolved in 1,000 parts by volume of solvent. The solution so obtained was diluted with further solvent to the desired lower concentrations.

2.5 ml of the solution of active compound were pipetted into a Petri dish. On the bottom of the Petri dish there was a filtered paper with a diameter of about 9.5 cm. The Petri dish remained uncovered until the solvent had completely evaporated. The amount of active compound per m<sup>2</sup> of filter paper varied with the concentration of the solution of active compound. After 25 test animals were then placed in the Petri dish and it was covered with a glass lid.

The condition of the test animals was continuously observed. The time which was necessary for 100% destruction was determined.

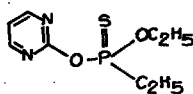
The test animals, the active compounds, the concentrations of the active compounds and the times at which there is 100% destruction can be seen from the following Table J.

TABLE J

(LT<sub>100</sub> test for diptera/*Musca domestica*)

| Active compound | Active compound concentration of the solution in % by weight | LT <sub>100</sub> in minutes (') or hours (hrs) |
|-----------------|--------------------------------------------------------------|-------------------------------------------------|
| [B]             | 0.02                                                         | 6 hrs                                           |
| (1)             | 0.02                                                         | 120'                                            |
| (3)             | 0.02                                                         | 80'                                             |
| (11)            | 0.02                                                         | 80'                                             |
| (10)            | 0.02                                                         | 95'                                             |
| (14)            | 0.02                                                         | 110'                                            |
| (5)             | 0.02                                                         | 120'                                            |
| (6)             | 0.02                                                         | 195'                                            |
| (2)             | 0.02                                                         | 100'                                            |
| (24)            | 0.02                                                         | 50'                                             |
| (25)            | 0.02                                                         | 90'                                             |

Example I.



17.2 g (0.1 mol) of O-ethyl-ethanethionophosphonic acid ester chloride were added to a suspension of 13.2 g (0.1 mol) of 2-hydroxypyrimidine hydrochloride and 34.5 g (0.25 mol) of potassium carbonate in 300 ml of acetonitrile. Thereafter, the reaction mixture was stirred for 3 hours at 50°C and then cooled to 20°C, and 600 ml of toluene were added. The mixture was extracted by shaking with twice

500 ml of water and the organic phase was separated off and dried over sodium sulphate. The solvent was then stripped off *in vacuo* and the residue was subjected to incipient distillation at 80°C. This gave 20 g (86% of theory) of O-ethyl-O-pyrimidin(2)yl-ethanethionophosphonic acid ester in the form of a yellow oil of refractive index  $n_D^{22}$ : 1.5283.

5

5

#### Examples 2—25.

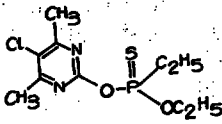
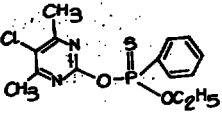
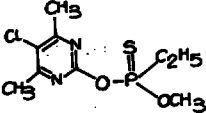
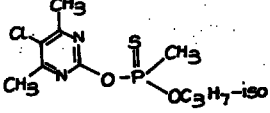
The following compounds were prepared analogously to Example 1.

| Example No. | Structure | Yield (% of theory) | Physical data (melting point °C; refractive index) |
|-------------|-----------|---------------------|----------------------------------------------------|
| 2           |           | 77                  | $n_D^{26}$ : 1.5310                                |
| 3           |           | 78                  | $n_D^{24}$ : 1.5358                                |
| 4           |           | 85                  | $n_D^{25}$ : 1.5194                                |
| 5           |           | 54                  | 56                                                 |
| 6           |           | 89                  | $n_D^{23}$ : 1.5203                                |
| 7           |           | 85                  | $n_D^{23}$ : 1.5774                                |
| 8           |           | 75                  | $n_D^{22}$ : 1.6006                                |
| 9           |           | 79                  | $n_D^{22}$ : 1.5833                                |
| 10          |           | 75                  | $n_D^{24}$ : 1.5468                                |

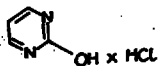
(Continued)

| Example No. | Structure | Yield (% of theory) | Physical data (melting point °C; refractive index) |
|-------------|-----------|---------------------|----------------------------------------------------|
| 11          |           | 79                  | $n_D^{24}$ : 1.5363                                |
| 12          |           | 89                  | $n_D^{24}$ : 1.5250                                |
| 13          |           | 73                  | $n_D^{24}$ : 1.5909                                |
| 14          |           | 64                  | $n_D^{24}$ : 1.5472                                |
| 15          |           | 62                  | $n_D^{24}$ : 1.5513                                |
| 16          |           | 48                  | $n_D^{27}$ : 1.5188                                |
| 17          |           | 52                  | $n_D^{26}$ : 1.5140                                |
| 18          |           | 68                  | $n_D^{26}$ : 1.5407                                |
| 19          |           | 73                  | $n_D^{24}$ : 1.5169                                |
| 20          |           | 59                  | $n_D^{24}$ : 1.5128                                |
| 21          |           | 52                  | $n_D^{24}$ : 1.5851                                |

(Continued)

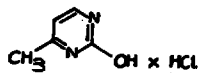
| Example No. | Styrene                                                                            | Yield (% of theory) | Physical data (melting point °C; refractive index) |
|-------------|------------------------------------------------------------------------------------|---------------------|----------------------------------------------------|
| 22          |   | 78                  | $n_D^{25}$ : 1.5085                                |
| 23          |   | 67                  | 54 – 56                                            |
| 24          |   | 75                  | $n_D^{24}$ : 1.5383                                |
| 25          |  | 58                  | $n_D^{25}$ : 1.5240                                |

The following exemplifies the preparation of the 2-hydroxypyrimidine derivatives (III) required as starting materials:

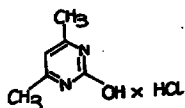


- 5 90 g (0.55 mol) of 1,1,3,3-tetra-methoxypropane were added to a solution of 30 g (0.5 mol) of urea in 350 ml of warm ethanol, and 100 ml of concentrated hydrochloric acid were then added dropwise to this mixture over the course of 1 to 2 hours. Whilst doing so, the temperature was kept at between 30 and 40°C; thereafter the mixture was stirred for a further 5 hours, at room temperature. After adding 500 ml of ether, the reaction product was filtered off. This gave 48.5 g (79% of theory) of 2-hydroxypyrimidine hydrochloride in the form of a yellow powder of melting point 198 to 201°C (with decomposition).

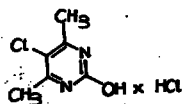
The following 2-hydroxypyrimidine derivatives were prepared analogously:



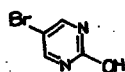
94% yield; melting point 236°C (decomposition)



80% yield; melting point 240°C (decomposition)

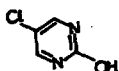


72% yield; melting point 210°C.



84 g (0.525 mol) of bromine were added to a solution of 66 g (0.5 mol) of 2-hydroxypyrimidine hydrochloride in 80 ml of water at room temperature. The mixture was then warmed to 70–80°C for 15 minutes, after which it was cooled to 5–10°C. The product which had precipitated was filtered off and rinsed with water. This gave 56 g (64% of theory) of 2-hydroxy-5-bromo-pyrimidine in the form of a colourless powder of melting point 250°C.

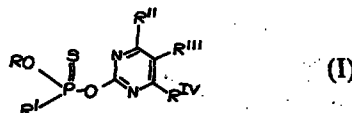
The following was prepared analogously:



45% yield; melting point 218°C (decomposition)

#### WHAT WE CLAIM IS:—

1. Pyrimidinylthionophosphonic acid esters of the general formula



in which

R represents alkyl with 1 to 6 carbon atoms,

R' represents alkyl with 1 to 6 carbon atoms or phenyl,

R'' and R<sup>IV</sup>, which can be the same or different, represent alkyl with 1 to 4 carbon atoms or hydrogen, and

R''' represents halogen or hydrogen.

2. Compounds according to claim 1 in which R represents alkyl with 1 to 4 carbon atoms, R' represents alkyl with 1 to 4 carbon atoms or phenyl, R'' and R<sup>IV</sup> represent hydrogen, methyl or ethyl, and R''' represents hydrogen, chlorine or bromine.

3. Each of the compounds according to claim 1 which are hereinbefore specifically identified in Examples 1 to 25.

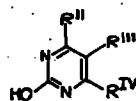
4. A process for the production of a compound according to any of claims 1 to 3 in which an O-alkylthionophosphonic acid ester halide of the general formula



in which

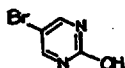
R and R' have the meanings given in claim 1 and

Hal represents halogen, is reacted with a 2-hydroxypyrimidine derivative of the general formula



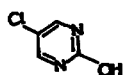
in which

R'', R''' and R<sup>IV</sup> have the meanings given in claim 1, in the form of the free base or the hydrochloride or an alkali metal salt, alkaline earth metal salt or ammonium salt.



84 g (0.525 mol) of bromine were added to a solution of 66 g (0.5 mol) of 2-hydroxypyrimidine hydrochloride in 80 ml of water at room temperature. The mixture was then warmed to 70–80°C for 15 minutes, after which it was cooled to 5–10°C. The product which had precipitated was filtered off and rinsed with water. This gave 56 g (64% of theory) of 2-hydroxy-5-bromo-pyrimidine in the form of a colourless powder of melting point 250°C.

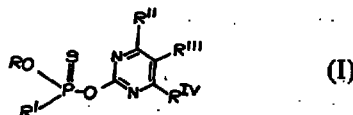
The following was prepared analogously:



45% yield; melting point 218°C (decomposition)

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1. Pyrimidinylthionophosphonic acid esters of the general formula



in which

R represents alkyl with 1 to 6 carbon atoms,

R' represents alkyl with 1 to 6 carbon atoms or phenyl,

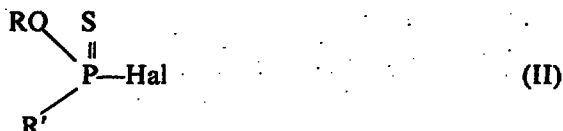
R'' and R''', which can be the same or different, represent alkyl with 1 to 4 carbon atoms or hydrogen, and

R'''' represents halogen or hydrogen.

2. Compounds according to claim 1 in which R represents alkyl with 1 to 4 carbon atoms, R' represents alkyl with 1 to 4 carbon atoms or phenyl, R'' and R''' represent hydrogen, methyl or ethyl, and R'''' represents hydrogen, chlorine or bromine.

3. Each of the compounds according to claim 1 which are hereinbefore specifically identified in Examples 1 to 25.

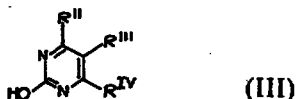
4. A process for the production of a compound according to any of claims 1 to 3 in which an O-alkylthionophosphonic acid ester halide of the general formula



in which

R and R' have the meanings given in claim 1 and

Hal represents halogen, is reacted with a 2-hydroxypyrimidine derivative of the general formula



in which

R'', R''' and R'''' have the meanings given in claim 1, in the form of the free base or the hydrochloride or an alkali metal salt, alkaline earth metal salt or ammonium salt.



5. A process according to claim 4 in which the compound of formula (II) is any of those hereinbefore specifically identified.
6. A process according to claim 4 or 5 in which the compound of formula (III) is any of those hereinbefore specifically identified.
- 5 7. A process according to any of claims 4 to 6 in which the reaction is carried out in the presence of a solvent. 5
8. A process according to any of claims 4 to 7 in which the reaction is carried out at 40 to 55°C.
9. A process for the production of a compound according to claim 1, substantially as hereinbefore described in any of Examples 1 to 25. 10
10. Compounds according to claim 1 whenever prepared by a process according to any of claims 4 to 9. 10
11. An insecticidal, acaricidal or nematocidal composition containing as active ingredient a compound according to any of claims 1 to 3 or 10 in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent. 15
12. A composition according to claim 11 containing from 0.1 to 95% of the active compound by weight.
13. A method of combating insect, acarid or nematode pests which comprises applying to the pests or a habitat thereof a compound according to any of claims 1 to 3 or 10 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 3 or 10 in admixture with a diluent or carrier. 20
14. A method according to claim 13 in which a composition is used containing from 0.0001 to 10% of the active compound, by weight. 25
15. Crops protected from damage by insects, acarids or nematodes by being grown in areas in which, immediately prior to and/or during the time of the growing, a compound according to any of claims 1 to 3 or 10 was applied alone or in admixture with a diluent or carrier. 25

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