PATENT SPECIFICATION

1,195,412

NO DRAWINGS

1,195,412

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COMPLETE SPECIFICATION

Pesticidal Preparations for Combating Mites

We, SCHERING AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Berghamen, 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:—

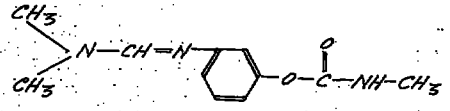
The present invention is concerned with pesticidal preparations for use against mites that are resistant to phosphoric acid esters, especially spinning mites that are plant parasites.

It has been known that mites (*Acarina*) and especially spinning mites (*Tetranychidae*) can become resistant to chemical materials used for combating them. This development of resistance is primarily brought about by materials based on phosphoric acid esters, which are among the best known and most effective acaricides. This has proved to be particularly serious because such a resistance of the pests is not only a resistance against the particular active substance used, but usually also a resistance against all other active substances which belong to the same class of compounds as the particular active substance. In addition, however, a resistance is also observed to active substances of other classes of compounds that exert their effect, like the active substance causing the resistance, by an inhibition of the cholinesterase enzyme in the animal body.

Of course, various ways have already been proposed for combating pests which have become resistant. In particular the manufacture and use of new compounds having a different mode of action has been proposed, but this does not exclude the possibility of a resistance, parallel to the first resistance, also being developed against such new active substances.

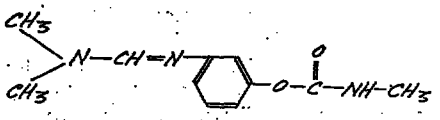
Furthermore, it has already been suggested some years ago to find compounds that are especially effective against resistant pests which have a higher sensitivity than non-resistant normal animals, this being described as so-called "Negative cross-resistance" (increased sensitivity induced by resistance). Hitherto, however, however only a few compounds having such properties have been found and these have been unable to find acceptance in practice because their effect as pesticides is unsatisfactory.

It has now been found that agents containing 3 - dimethylaminomethyleneimino-phenyl-N-methyl carbamate of the formula



and/or their salts with inorganic or organic acids exhibit, alongside their already known effect against insects and normally sensitive mites, an increased action against mites that are resistant to phosphoric acid esters, especially spinning mites that are plant parasites, and are therefore suitable for combatting these pests with a smaller amount of material than is usual for normally sensitive mites.

Accordingly, the present invention provides a pesticidal preparation which comprises as the active ingredient 3 - dimethylaminomethyleneimino - phenyl - N - methyl carbamate of the formula



and/or an acid addition salt thereof, in admixture or conjunction with a carrier, the concentration of the active ingredient being at

most 0.004 per cent calculated on the weight of the preparation.

The present invention also provides a method of combating mites on a living plant, wherein a living plant is treated with a pesticidal preparation as defined above.

The present invention further provides a method of combating mites in a crop area, wherein a crop area is treated with a pesticidal preparation as defined above.

The insecticidal and acaricidal effects of the compound of the above formula, as well as of its salts, have admittedly already been known from German Patent Specification No. 1,169,194 (British Patent Specification No. 987,381). However conclusions as to an effect especially exerted against mites that are resistant to phosphoric acid esters could not have been drawn from these known effects, because no such effect has hitherto been discovered in insecticidal and acaricidal compounds of analogous constitution. Furthermore it is surprising, and must be considered as an extremely rare phenomenon, that the discovered effect against mites that are resistant to phosphoric acid esters is even evident in use at concentrations which are below the amounts usually required in practice for combating non-resistant, that is normally sensitive, mites. The discovery that mites that are resistant to phosphoric acid esters can be combatted with lesser, and hence more economical, amounts of the active ingredient used in accordance with the present invention than can non-resistant mites may, therefore, be considered an important inventive achievement.

By usual amounts required in practice there are to be understood herein concentrations of about 20 to 50 grams per 100 litres of spraying liquor, which when using known acaricides based on phosphoric acid esters for combatting pests that have become resistant frequently even have to be exceeded several-fold in order to achieve successful results in combating the pests.

As compared with this, the preparations of the present invention make it possible to combat mites that are resistant to phosphoric acid esters successfully at lower and hence more economical concentrations, and this represents a significant technical advance. By resistant spinning mites which can be combatted with the preparations of the invention there are especially to be understood those which show mortality rates LG_{50} of at least 50 ppm (parts by weight of active substance per million) against acaricidally active phosphoric acid esters.

The preparations of the present invention may contain the compound of the above formula as the sole active ingredient or may contain this active ingredient in admixture or together with other pesticides such as acaricides, insecticides or fungicides. The preparations are formulated in one of the forms normally employed for plant protection, using liquid or solid carriers. Suitable liquid carriers, in addition to water, are, for example, mineral oils or solvents; suitable solid carriers are, for example, bentonite, Fuller's earth, gypsum, chalk, kieselguhr, pyrophyllite, silicon dioxide, talc or flours of vegetable origin such as those made from cotton seed or nut shells. The preparations may contain additives such as emulsifiers wetting agents, binders, stabilisers, propellants, scents, attraction substances or repellents. The preparations may be in the form of, *inter alia*, liquids capable of being atomised, sprayed or squirted, such as suspensions, emulsions or solutions.

The active substance of the above formula is, as has already been mentioned, known *per se* and may be manufactured by methods which are known *per se*.

The active substance used in the preparations of this invention may be used as such and/or in the form of its salts with inorganic or organic acids, for example the water-soluble hydrochlorides.

As has already been mentioned, smaller concentrations than usual are sufficient for combating mites that are resistant to phosphoric acid esters, for example, 2 grams of active substance per 100 litres of spraying liquor, as may be seen from Example 3.

The following Examples describe experiments showing the effect of the preparations of the present invention in comparison with known acaricides.

Example 1

The following Table I contains the LC_{50}-values (lethal concentration for 50% mortality) which were obtained for female spinning mites by means of the leaf piece method. In order to obtain these results, round pieces of leaf of diameter 18 mm were punched out of bean leaves, laid with the rear side uppermost on round foam supports in Petri dishes filled with water, and 10 female spining mites were placed on each. Treatment was carried out with 4 mg of spraying liquor per cm^2, there being used four concentrations, in each case reducing by half, near the LC_{50}-value to be expected in each case. 4 leaf pieces having a total of 40 animals were used at each concentration, and the mortality values were calculated after 3 to 4 days as a percentage of the dead animals relative to the total number of experimental animals and were plotted on a so-called log-probit paper (probability grid). A straight line was drawn through the various points and the 50% mortality values were read off as a percentage of the active substance. The following were used as spinning mites:

a) a normally sensitive laboratory strain of the greenhouse spinning mit (*Tetranychus urticae Koch*)=N

b) a strain of the carnation spinning mite generally resistant to phosphoric acid esters (*Tetranychus dinathica Dosse*)= SR

c) a resistant strain obtained by selection with O,O-dimethyl - S - 2 - (ethylsulphinyl)-ethylthiol phosphate=MR.

TABLE I

Active Substances	LC_{50} in ppm N	SR	MR
3-Dimethylaminomethyleneiminophenyl-N-methyl carbamate	2.9	0.21	0.34
Phosphoric acid esters:			
O,O-Dimethyl-S-2-(ethylsulphinyl)-ethyl thiol phosphate	0.6	250	330
O,O-Diethyl-O-(2-isopropyl-4-methylpyrimidyl-(6))-thionophosphate + O,O-Diethyl-2,5-di-chlorophenylmercaptomethyl-dithiophosphate (5:1)	10		500
O,O-Dimethyl-N-methylcarbamoylmethyldithio-phosphate	1		68
O,O-Diethyl-S-(3,4-dihydro-4-oxo-(1,2,3-benzotriazinyl-(3))dithiophosphate	1	80	
O,O-Dimethyl-S-(3,4-dihydro-4-oxo-(1,2,3-benzotriazinyl-(3))-dithiophosphate	6	100	
O,O-Diethyl-N-isopropylcarbamoylmethyl-dithiophosphate	0.8	600	
O,O-Dimethyl-S-(5-methoxy-1,3,4-thiadiazol-2-onyl-(3)-methyl)-dithiophosphate	0.6	80	
Carbamates:			
4-Methylmercapto-3,5-dimethylphenyl-methyl-carbamate	13	122	55
4-Dimethylamino-3,5-dimethylphenylmethyl-carbamate	25		140

EXAMPLE 2

The Table II below summarises the LC_{50}-values which were obtained on treating freshly laid spinning mite eggs and thereby killing the larvae which slid out of the eggs (ova-larvicidal effect). For this purpose, female spinning mites were placed on the leaf pieces and left thereon for 24 hours in order to lay eggs. About 100 to 150 eggs on 3 leaf pieces were obtained from 30 female animals. After removing the female animals the specimens were treated with 4 mg of spraying liquor per cm^2, there being used four concentrations, in each case reducing by half, near the LC_{50}-value to be expected in each case. The mortality of the young larvae was observed 2 days after sliding had been verified in the untreated controls, or 7 days after treatment. The further evaluation was carried out as described in Example 1.

TABLE II

Active Substances	N	LC_{50} in ppm SR	MR
3-Dimethylaminomethyleneiminophenyl-N-methyl carbamate	21	3	3.7
O,O-Dimethyl-S-2-(ethylsulphinyl)-ethylthiol-phosphate	7	approxi-mately 4000	approxi-mately 5000
O,O-Diethyl-S-(3,4-dihydro-4-oxo-(1,2,3-benzotriazinyl-(3)-dithiophosphate	7.4	40	

EXAMPLE 3

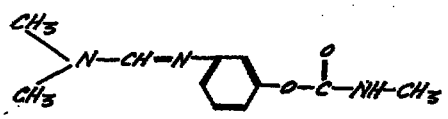
Potted bush bean plants in the 2-leaf stage were infected with all development stages of the spinning mites and were sprayed after 2 days with a solution or emulsion of the material to be tested, so as to be dripping wet on all sides. The plants were then transferred to a greenhouse and after the first 3-sectioned small leaf had grown through, which took place after 10 days, the attack (B) on these leaves was estimated in terms of the percentage proportion of the whitish sucking spots relative to the total leaf area. The estimated values were converted into effect values (W) (W%=100−B%).

TABLE III

Active Substances	Concentration	Effect as a % N	MR	SR
3-Dimethylaminomethyleneiminophenyl--N-methyl carbamate hydrochloride	0.004%	96	100	100
	0.002	70	100	100
	0.001	41	97	99
	0.0005	12	94	99
	0.00025	—	51	82
	0.000125	—	—	78
O,O-Dimethyl-S-2-(ethylsulphinyl)-ethylthiolphosphate	0.4%	—		96
	0.2	—		90
	0.1	—		10
	0.05	—		0
	0.002	98		—
	0.001	97		—
	0.0005	90		—
	0.00025	23		—

WHAT WE CLAIM IS:—

1. A pesticidal preparation which comprises as the active ingredient 3 - dimethylamino-methyleneimino-phenyl-N-methyl carbamate of the formula



and/or an acid addition salt thereof, in admixture or conjunction with a carrier, the concentration of the active ingredient being at most 0.004 per cent calculated on the weight of the preparation.

2. A pesticidal preparation as claimed in claim 1, which is in the form of a spraying liquor and contains up to 4 grams of the active ingredient per 100 litres of the preparation.

3. A method of combating mites on a living plant, wherein a living plant is treated with a preparation as claimed in claim 1 or 2.

4. A method as claimed in claim 3, and

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	0.2	—		90
	0.1	—		10
	0.05	—		0
	0.002	98		—
	0.001	97		—
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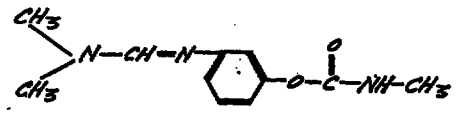

and/or an acid addition salt thereof, in admixture or conjunction with a carrier, the concentration of the active ingredient being at most 0.004 per cent calculated on the weight of the preparation.

2. A pesticidal preparation as claimed in claim 1, which is in the form of a spraying liquor and contains up to 4 grams of the active ingredient per 100 litres of the preparation.

3. A method of combating mites on a living plant, wherein a living plant is treated with a preparation as claimed in claim 1 or 2.

4. A method as claimed in claim 3, and

conducted substantially as described in Example 3 herein.

5. A method of combating mites in a crop area, wherein a crop area is treated with a preparation as claimed in claim 1 or 2.

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