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3,502,778

MITICIDES

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3 Claims

ABSTRACT OF THE DISCLOSURE

Miticidal agents containing a 3-dimethylamino-methyl-
eneimino-phenyl-N-methyl carbamate, or their salts with
inorganic or organic acids have an increased effect against
phosphoric ester-resistant mites and other insects.

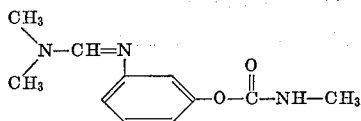
This invention concerns an agent with an increased
effect against phosphoric ester-resistant mites, particu-
larly phytoparasitic spider mites.

It is known that mites, (Acarina), and particularly
spider mites, (Tetranychidae), become resistant to chem-
ical agents which are used for their control. This re-
sistance is built up by agents particularly on the basis
of phosphoric esters, which belong to the best known and
most effective acaricides. It was disconcerting that such
resistance of the pests is directed not only against the
active substance used, but against all other active sub-
stances which belong to the same class of compounds.
Beyond that, a resistance is also observed against active
substances of other compound classes provided they dis-
play their resistance, just like the resistance-causing active
substance, apparently due to the inhibition of the choli-
nesterase enzyme in the animal body.

Various methods have already been shown to control
pests that have become resistant. Thus, it was sug-
gested in particular to reduce and apply compounds with
a different mode of action, which does not exclude, how-
ever, that resistance can also develop against such new
active substance, parallel to the former.

It was suggested several years ago to find compounds
which are particularly effective against resistant pests
that show a higher sensitivity than non-resistant normal
animals, which is called "negative cross resistance," i.e.,
increased sensitivity induced by resistance. So far, how-
ever, only a few compounds having such properties have
been found, which could not assert themselves in practice,
because their effect as pest control agents was not satis-
factory.

It was found that agents containing 3-dimethylamino-
methyleneiminophenyl-N-methyl carbamate of the formu-
la:



and/or their salts with inorganic or organic acids, in ad-
dition to their known effect against insects, and normally
sensitive mites, also show an increased effect against phos-
phoric ester-resistant mites, particularly phytoparasitic
spider mites. Such agents are therefore suitable for the
control of these pests in an amount which is less than
that generally used for normal sensitive mites.

The insecticidal and acaricidal effect of the above men-
tioned compound as well as of its salts is already known

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from German Patent No. 1,169,194 and British Patent
No. 987,381. Inferences on an effect, particularly against
phosphoric ester-resistant mites, could not be drawn, how-
ever, from this known effect, because no such effect was
found so far in insecticidal and acaricidal compounds of
a similar constitution. Besides, it is a surprising and ex-
tremely rare phenomenon that the observed effect against
phosphoric ester-resistant mites already sets in with con-
centrations which are usually below the amount necessary
in practice to control non-resistant, that is, normal re-
sistant mites. The finding that phosphoric ester-resistant
mites can already be controlled with a smaller, and thus
more economical, amount of the substances to be used
according to the invention that non-resistant mites must
therefore be considered a particularly inventive achieve-
ment.

By usual amounts we understand application concen-
trations of about 20 to 50 g. per liter spray broth, which
must frequently be exceeded by a multiple when using
known acaricides on the basis of phosphoric esters for
the control of resistant pests, in order to ensure positive
results.

The agent according to the invention, on the other
hand, permits the successful controls of phosphoric ester-
resistant mites with a lower and thus more economical
concentration, which represents considerable technical
progress. Resistant spider mites which can be controlled
according to the invention are particularly those which
show mortality values LC₅₀ of at least 50 p.p.m. (parts
by weight active substance per million), compared to
acaricidal phosphoric esters.

The agent according to the invention can be used per
se in conjunction with other pest control agents, such as
acaricides, insecticides or fungicides. Its preparation is ef-
fected in a manner customary for plant-protectives, using
liquid or solid vehicles. Suitable liquid vehicles are, in
addition to water, mineral oils or solvents; solid vehicles
are, for example, bentonite, bleaching earth, gypsum,
lime, kieselguhr, pyrophyllite, silicon dioxide, talcum, or
flours of vegetable origin, such as from cotton seeds or
nut shells. The preparations may contain additives, such
as emulsifiers, wetting agents, binders, stabilizers, pro-
pellant gases, odoriferous substances, attractants or re-
pellents. The agents can be used among others as atom-
izable or sprayable substances, such as suspensions, emul-
sion or solutions.

The active substance, as mentioned above, is known
in itself and can be produced according to methods known
in the art.

The active substance to be used according to the inven-
tion can be applied as such and/or in the form of its salts
with inorganic or organic acids, for example, the water-
soluble hydrochlorides.

The content of active substance in the various prepara-
tions can vary within wide limits. It depends, among
others, on the type of formulation and on the application
method and amounts to about 0.1 to 90% by weight of
the agent. As mentioned above, lower concentrations than
usual are sufficient for the control of phosphoric ester-
resistant mites. For example, 2 g. of active substance per
100 liter spray broth can be used as can be seen from
Example 3, an increase up to 10 g. active substance per
100 liter spray broth already including the safety margin
customary in practice.

The following illustrative examples will show the effect
according to the invention, compared to the known acari-
cides.

EXAMPLE 1

The following table contains the LC₅₀ values (lethal
concentration with 50% mortality) which were obtained
for female spider mites by means of the leaf piece method.

To this end, round leaf pieces with a diameter of 18 mm., punched out from bean leaves, were placed with the back-side up on round foam supports in water-filled Petri-dishes in each of which were put 10 female spider mites. The treatment was effected with 4 mg. spray broth per qcm., using four concentrations, each decreasing by half, in the proximity of the anticipated LC-50 value. For each concentration, 4 leaf pieces were used with a total of 40 animals. The mortality values were calculated after 3 to 4 days in percent of the dead animals to the total sum of the test animals, and entered on so-called Log-Probity-paper (probability grading). Through the respective points, a line was drawn and the value of the 50% mortality read in percent active substance. As spider mites were used (a) a normal sensitivity laboratory strain of the greenhouse spider mite (*Tetranychus urticae* Koch)=N; (b) a general phosphoric-ester resistant strain of the carnation spider mite (*Tetranychus dinathica* Dosse)=SR; (c) a resistant strain obtained by selection with O,O-dimethyl-S-2-(ethyl-sulfinyl)-ethyl thiophosphate=MR.

Active Substance	LC/50 in p.p.m.		
	N	SR	MR
3-dimethylaminomethyleniminophenyl-N-methylcarbamate	2.9	0.21	0.34
Phosphoricester:			
O,O-dimethyl-S-2-(ethylsulfinyl)-ethylthiophosphate	0.6	250	330
O,O-diethyl-S-(2-isopropyl-4-methyl)-pyrimidyl-(6)-thionophosphate+O, 0-diethyl-2,5-dichlorophenylmercaptomethyl-N-methylcarbamoylmethylthiophosphate (5:1)	10	-----	500
O,O-dimethyl-N-methylcarbamoylmethylthiophosphate	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-isopropylcarbamoylmethylthiophosphate	0.8	600	-----
O,O-dimethyl-S-(5-methoxy-1,3,4-thiadiazol-2-on-yl-(3)-methyl)-dithiophosphate	0.6	80	-----
Carbamates:			
4-methylmercapto-3,5-dimethylphenylmethylcarbamate	13	122	55
4-dimethylamino-3,5-dimethylphenylmethylcarbamate	25	-----	140

EXAMPLE 2

In this table, the LC₅₀ values are compiled which are obtained in the treatment of fresh-laid spider mite eggs by killing the larvae emerging from the eggs (ovolarvicidal effect). To this end, female spider mites were placed on leaf pieces and left there for 24 hours to lay their eggs.

About 100 to 150 eggs were obtained on 3 leaf pieces from 30 females. After removing the females, the treatment was effected with 4 mg. spray broth per qcm., four concentrations, each decreasing by half, being used in the proximity of the anticipated LC₅₀ value. The observation of the mortality of the young larvae was made 2 days after the proven emergence in the untreated controls and 7 days respectively actively after the treatment. The further evaluation was effected as described in Example 1.

Active substances	LC-50 in p.p.m.		
	N	SR	MR
3-dimethylaminomethyleniminophenyl-N-methylcarbamate	21	3	3.7
O,O-dimethyl-S-2-(ethylsulfinyl)-ethylthiophosphate	7	ca.4,000	ca.5,000
O,O-diethyl-S-(3,4-dihydro-4-oxo)-1,2,3-benzotriazinyl-(3)-dithiophosphate	7.4	40	-----

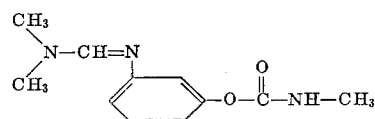
EXAMPLE 3

Potted bush bean plants in the 2-leaf stage were infected with all stages of the spider mites and sprayed on all sides dripping wet after 2 days with a solution and emulsion respectively of the agent to be tested. Then the plants were brought into the greenhouse and after washing the first 3-part leaflet, which was done after 10 days, the attack (B) on these leaves being estimated on the basis of the percentual portions of the white suction sports in the total leaf area. The estimated values were converted to effect (W). (W%) = 100 - B%.

Active substances	Conc., percent	Effect in percent		
		N	MR	SR
3-dimethylaminomethyleneiminophenyl-N-methylcarbamatehydrochloride.	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-(ethylsulfinyl)-ethylthiophosphate.	0.4	-----	-----	96
	0.2	-----	-----	-----
	0.1	-----	-----	10
	0.05	-----	-----	0
	0.002	98	-----	-----
	0.001	97	-----	-----
	0.0005	90	-----	-----
	0.00025	23	-----	-----

What is claimed is:

1. A method of combating phosphoric ester resistant, phytoparasitic spider mites, comprising applying an effective amount of a spray broth containing as the active substance 3 - dimethylaminoethyleneiminophenyl N - methyl carbamate of the formula



or the hydrochlorides thereof onto infected plants, the amount of said active substance in the spray broth being in the range between 0.1 and 90% by weight thereof.

2. The method of claim 1 wherein the active substance is a hydrochloride.

3. The method of claim 1 wherein active substance is applied in a concentration of from about 2 grams to about 10 grams per 100 liters of spray broth.

References Cited

UNITED STATES PATENTS

3,336,186 8/1967 Peissker et al. ----- 167-30

ALBERT T. MEYERS, Primary Examiner

F. E. WADDELL, Assistant Examiner