

PATENT SPECIFICATION

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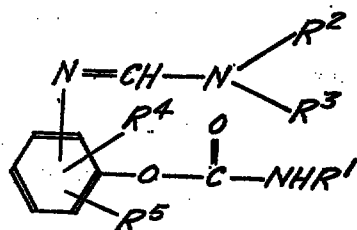


(54) PESTICIDAL PREPARATIONS

(71) We, SCHERING AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, 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 having an increased activity, containing mixtures of carbamates and formamidines.

British Specification No. 987,381 has described and claimed preparations having insecticidal and acaricidal activities, which contain carbamates of the general formula (1)



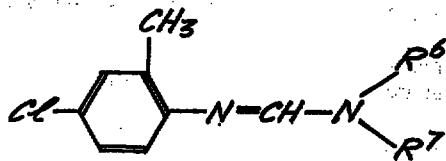
(1)

in which

R¹ represents an alkyl or cyclohexyl group, R² and R³ each represents an alkyl group or R² + R³ together with the nitrogen atom represent a cyclic group that may contain one or more further hetero atoms, and

R⁴ and R⁵ each represents a hydrogen or halogen atom or an alkyl or alkenyl group.

Furthermore, it has been known from British Specification No. 1,039,930 that preparations containing formamidines of the general formula (2)



(2)

in which R⁶ and R⁷ each represents an alkyl group containing up to 4 carbon atoms, or R⁶ represents a hydrogen atom and R⁷ represents an alkyl group containing up to 4 carbon atoms, and their salts, have good acaricidal and especially acaricidal/ovicidal properties.

The present invention is based on the observation that pesticidal preparations that contain at least one carbamate of the above general formula (1) in admixture or conjunction with at least one formamidine of the above general formula (2) have a greater effect upon vegetable and animal parasites than the cumulative effect of the single components used alone.

This activity, which substantially surpasses the activity of the single components, is surprising and could not have been foreseen because at the present time it is not possible to make any predictions in the absence of knowledge of the mechanism on which this activity depends.

Accordingly, the present invention provides a pesticidal preparation which comprises a carbamate of the general formula (1) as defined above, or a salt thereof, in admixture or conjunction with a formamidine of the general formula (2) as defined above, or a salt thereof. If desired, the preparation may contain at least two carbamates of the general formula (1) as defined above or salts thereof; the preparations may also contain at least two formamidines of the general formula (2) as defined above or salts thereof.

The use of the new preparations of this invention offers substantial advantages because to achieve an equivalent effect against many pests a smaller quantity of active substance is needed than when the components are used singly. Therefore pests can be controlled in a more successful, safe and economic manner and it is possible, for example, to reduce substantially the waiting periods between treatment and harvesting.

A special advantage of the preparations of this invention is their increased effect upon all development stages of mites that appear as parasites on plants and animals because this

is the only way of controlling them successfully. This effect is unexpected because with all acaricides previously known to us the main effect is found either only against the mobile stages of the pests (adulticidal effect) or against their ova and in most cases also their larvae (ovicidal effect). A mite population of, for example, species of the Tetranychidae family consists always of various stages of development, and mobile stages are always found side by side with ova so that it is often possible for new generations of the pests to emerge even after a short time either from the undamaged ova or from the mobile stages.

The preparations of this invention not only

overcome this disadvantage of the acaricides previously known to us but in addition they have a more potent effect against both stages, and this constitutes an appreciable technical advantage.

Moreover, it has been observed that the preparations of this invention are also superior in their effect as acaricides and/or acaricides/ovicides to acaricides previously known to us, as is revealed by the comparative tests shown below.

The individual components used in the preparations of this invention are primarily the following active substances or their salts with inorganic or organic acids:

A. Carbamates

No.	Compound	Physical constant
1	3-dimethylaminomethyleniminophenyl-N-methylcarbamate	m.p. 102 — 103°C
2	4-dimethylaminomethyleniminophenyl-N-methylcarbamate	m.p. 82 — 85°C
3	4-dimethylaminomethylenimino-3-methylphenyl-N-methylcarbamate	m.p. 110°C
4	4-diethylaminomethylenimino-3-methylphenyl-N-methylcarbamate	m.p. 178 — 179°C (hydrochloride)
5	4-dimethylaminomethylenimino-3-methylphenyl-N-ethylcarbamate	oil
6	4-dimethylaminomethylenimino-2-allylphenyl-N-methylcarbamate	m.p. 120 — 121°C (chloracetate)
7	4-dimethylaminomethylenimino-3,5-dimethylphenyl-N-methylcarbamate	m.p. 156 — 157°C
8	4-diethylaminomethylenimino-3,5-dimethylphenyl-N-methylcarbamate	m.p. 86 — 87°C
9	4-dimethylaminomethylenimino-3-methyl-6-isopropylphenyl-N-methylcarbamate	m.p. 127.5—128°C
10	4-diethylaminomethylenimino-3-methyl-6-isopropylphenyl-N-methylcarbamate	m.p. 92 — 92.5°C
11	4-diethylaminomethylenimino-2-methyl-5-isopropylphenyl-N-methylcarbamate	m.p. 187 — 188°C (hydrochloride)
12	4-dimethylaminomethylenimino-3-methyl-5-isopropylphenyl-N-methylcarbamate	m.p. 103 — 104.5°C
13	4-diethylaminomethylenimino-3-methyl-5-isopropylphenyl-N-methylcarbamate	oil
14	4-(N',N'-tetramethylenaminomethylenimino)-3,5-dimethylphenyl-N-methylcarbamate	m.p. 185°C

A. Carbamates (Continued)

No.	Compound	Physical constant
15	4-(N',N'-pentamethylenaminomethylenimino)-3,5-dimethylphenyl-N-methylcarbamate	m.p. 85.0°C
16	4-morpholinomethylenimino-3,5-dimethylphenyl-N-methylcarbamate	m.p. 144 — 145°C
17	3-dimethylaminomethylenimino-4-methylphenyl-N-methylcarbamate	m.p. 118 — 119°C
18	3-dimethylaminomethyleniminophenyl-N-butylcarbamate	m.p. 61 — 65°C
19	4-dimethylaminomethyleniminophenyl-2-chlorophenyl-N-methylcarbamate	m.p. 118 — 119°C (chloracetate)
20	4-dimethylaminomethylenimino-3-methylphenyl-N-cyclohexylcarbamate	m.p. 100 — 103°C
21	4-dimethylaminomethyleniminophenyl-N-ethylcarbamate	m.p. 105 — 108°C
22	4-dimethylaminomethyleniminophenyl-N-butylcarbamate	oil n_D^{24} = 1.5450
23	4-dimethylaminomethyleniminophenyl-3,5-dimethylphenyl-N-ethylcarbamate	m.p. 146 — 147°C

B. Formamidines

1	N-(2-methyl-4-chlorophenyl)-N'-methylformamidine
2	N-(2-methyl-4-chlorophenyl)-N',N'-dimethylformamidine
3	N-(2-methyl-4-chlorophenyl)-N',N'-dimethylformamidinium chloride
4	N-(2-methyl-4-chlorophenyl)-N',N'-diethylformamidine
5	N-(2-methyl-4-chlorophenyl)-N'- <i>n</i> -propylformamidine
6	N-(2-methyl-4-chlorophenyl)-N',N'-di- <i>n</i> -propylformamidine
7	N-(2-methyl-4-chlorophenyl)-N'-isobutylformamidine
8	N-(2-methyl-4-chlorophenyl)-N'-secondary butylformamidine

The active compounds in the preparations of this invention may be used alone or in conjunction or admixture with other pesticides, such as insecticides, acaricides or fungicides. The preparations of the present invention may take the usual form of plant protection preparations containing liquid or solid carriers. Suitable liquid carriers are, *inter alia*, water,

mineral oils or solvents; suitable solid carriers are, for example, bentonite, bleaching earth, gypsum, lime, kieselguhr, pyrophyllite, silica or talcum. The preparations may also contain further additives such as emulsifiers, wetting or binding agents, propellant gases, perfumes, stabilizers, pest attracting substances or repellents. The preparations may be used, *inter*

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alia, as dusting or dispersing agents or granulates, as sprayed, sprinkled or atomized liquids, or as aerosols or fumigants.

5 The combination of the carbamates and formamidines of the general formulae (1) and (2), respectively, incorporated in pesticidal and plant protecting preparations, for example in insecticides or acaricides, may vary within wide limits and depends among other things on the ratio of the components, on the type of preparation, on the manner of application, the desired control effect and on the kind of pest to be controlled. Depending on the form of application the concentration of the combination in the preparation may be 10 from about 0.1 to 90% by weight calculated on the weight of the preparation as a whole, and may be as low as 0.001% by weight. In general, 15 however, working concentrations between about 0.025 and 10% in liquid or solid carriers produce excellent results. For some purposes a working concentration up to about 25% by weight may be desirable.

20 In the preparations of this invention the weight ratio of the carbamate A to the formamidine B may as a rule vary from 1 to 5:1 to 10.

25 Particularly good results are achieved with a weight ratio of carbamate A : formamidine B of 1 : 1 to 1 : 2.

30 The active compounds contained in the new preparations of this invention may be used as such, or in the form of their salts, for example of the water-soluble hydrochlorides.

35 These compounds which, as mentioned above, are known *per se* may be prepared in a known manner.

40 The preparations of the present invention containing the aforesaid active substances are prepared in the usual manner, for example in mills or mixers.

45 Among the above-mentioned essential components of the preparations of the present invention the following active substances have proved particularly valuable for controlling plant parasites (mites): 3 - Dimethylamino-methyleniminophenyl - N - methylcarbamate and 4 - dimethylaminomethylenimino - 3-methylphenyl - N - methylcarbamate (designated as compounds A 1 and A 3 in the 50 Tables below) and N - (2 - methyl - 4 - chlorophenyl) - N,N' - dimethylformamidine (designated as compounds B 2 in the Tables below) and their salts, especially the hydrochlorides. 55 A preferred weight ratio of carbamate A 1: formamidine B 2 (or their salts) is 1 : 2 and of carbamate A 3 : formamidine B 2 (or their salts) is 1 : 1.

60 As stated above, it is a particularly impor-

tant advantage of the preparations according to the present invention that they act against insects and other pests as well as against their ova so that they lend themselves to a wide variety of uses.

As examples of pests that can be controlled with good results the following may be mentioned:

Codling moth (*Carpocapsa pomonella*),
peach borer (*Cydia molesta*),
peach moth (*Anarsia lineatella*),
summer fruit tortrix moth (*Capua reticulana*),
prune saw fly (*Hoplocampa hapla* and *minuta*),
apple flea (*Psylla mali*),
aphids (*Empoasca* sp.),
San José scale (*Quadraspidiotus perniciosus*)
and
moths (*Leucopetra scitella* and *Lithocolletis blancardella*).

The unexpected superiority of the combination of the active components used in the preparations of the present invention as compared with the single components is revealed by the experiments described in the Examples below.

The present invention also provides a method of controlling pests in a crop area, wherein the crop area is treated with a preparation according to the present invention.

The present invention further provides a method of controlling pests in a commercially reared animal, wherein a preparation according to the present invention is applied to a commercially reared animal.

The following Examples illustrate the invention:

EXAMPLE 1

In 7 field tests with numerous repetitions in cultivated apple trees carried out for the purpose of determining the degree of control of the fruit tree ermine moth (*metatetranychus ulmi* Koch) the results listed in Table I below were recorded; in these evaluations the mixed products were accorded the value of 100 and the effects of the single components are shown as percentages thereof. The preparations tested contained 3 - dimethylaminomethyleniminophenyl - N - methylcarbamate (A 1) and N - (2 - methyl - 4 - chlorophenyl) - N,N' - dimethylformamidine (B 2) in the weight ratio of 1:2, or 4 - dimethylaminomethylenimino - 3 - methylphenyl - N - methylcarbamate (A 3) and N - (2 - methyl - 4 - chlorophenyl) - N,N' - dimethylformamidine (B 2) in the weight ratio of 1:1, and the results obtained were compared with those obtained with preparations containing the single components. The preparations were applied in the form of aqueous suspensions.

TABLE I

Preparation contains	The weight ratio of A : B	Active substance in 100 litres of spray broth in grams	Evaluation of effect achieved
A 1+B 2	1 : 2	75	100
A 3+B 2	1 : 1	80	100
A 1		75	79.6
A 3		80	82.2
B 2		80	75.8

EXAMPLE 2

5 The following Table II gives the LC₅₀ values of preparations of this invention and of a few hitherto known acaricides. These values were determined by tests using round pieces (18 mm diameter) of bean leaves punched out from the leaves, which were placed upside down on a sheet of foam material in 10 Petri dishes filled with water, and each piece was infested with 10 female spider mites. For the ovicidal tests the ova were obtained by leaving the female mites for 24 hours on the test pieces and then removing them. The mites 15 and their ova were treated with 4 mg of spray broth per cm², using in each case 3 to 4 concentration steps within the anticipated LC₅₀ range. In the adult tests 4 pieces of leaves infested with a total of 40 adults, and for the 20 ovicide tests 3 pieces of leaves infested with about 200 ova were used, and the mortality values were calculated after 3 to 4, and 7 days respectively, (these mortality values represent-

ing the number of the killed mites expressed as a percentage of the total number of mites used in the test) and plotted on so-called Log-Probit paper (probability ordinates and abscissae). A line drawn through all the points represented a straight line and the 50% mortality values were read off in terms of the percentage of the active substance. 25 30

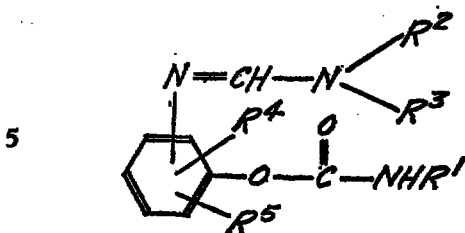
The superiority of the preparations of this invention which contain 3 - dimethylamino-methyleniminophenyl - N - methylcarbamate (A 1) to 4 - dimethylaminomethylenimino- 35 3 - methylphenyl - N - methylcarbamate (A 3), in each case in admixture with N - (2-methyl-4 - chlorophenyl) - N',N' - dimethylformamidine (B 2) in a weight ratio of 1:2 and 40 1:1, respectively, is unquestionable because, in contradistinction to the reference preparations, an approximately equivalent effect is achieved upon all stages of the pests.

TABLE II

Preparation contains Mixture according to this invention	Weight ratio	LC ₅₀ in parts per million	
		adulticidal effect	ovicidal effect
A 1+B 2	1 : 2	8.1	11.25
A 3+B 2	1 : 1	12.2	15.7
Single components			
A 1		2.9	21.4
A 3		8	about 40
B 2		62	6.7
Reference preparations			
0,0-dimethyl-S-2(ethylsulphinyl)- ethylthiophosphate		0.75	24
0,0-dimethyl-N-methylcarbamoyl- methylthiophosphate		2.3	27
0,0-dimethyldiethylamido-1- chloro-crotonylphosphate		3.7	200
0,0-diethyl-2-isopropyl-4-methyl- 6-pyrimidinyl-thiophosphate		14	about 400
0,0-diethyl-p-nitrophenyl-thiophosphate		13.7	310
1,1-bis-(p-chlorophenyl)-2,2,2-trichlorethane		19	82
2,4,5,4'-tetrachlorodiphenylsulphone		2000	1.2
p-chlorophenyl-p-chlorobenzene-sulphonate		2000	20

WHAT WE CLAIM IS:—

1. A pesticidal preparation which comprises a carbamate of the general formula

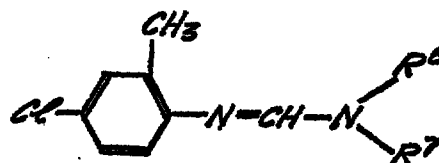


in which

R¹ represents an alkyl or cyclohexyl group,
R² and R³ each represents an alkyl group

or R²+R³ together with the adjacent nitrogen atom represent a cyclic group that may contain a further hetero atom, and

R⁴ and R⁵ each represents a hydrogen or halogen atom or an alkyl or alkenyl group, or a salt thereof, in admixture or conjunction with a formamidine of the general formula



in which



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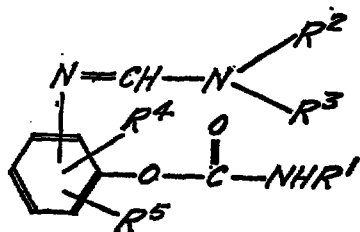
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TABLE II

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A 1+B 2	1 : 2	8.1	11.25
A 3+B 2	1 : 1	12.2	15.7
<u>Single components</u>			
A 1		2.9	21.4
A 3		8	about 40
B 2		62	6.7
<u>Reference preparations</u>			
0,0-dimethyl-S-2(ethylsulphinyl)- ethylthiophosphate		0.75	24
0,0-dimethyl-N-methylcarbamoyl- methylthiophosphate		2.3	27
0,0-dimethyldiethylamido-1- chloro-crotonylphosphate		3.7	200
0,0-diethyl-2-isopropyl-4-methyl- 6-pyrimidinyl-thiophosphate		14	about 400
0,0-diethyl-p-nitrophenyl-thiophosphate		13.7	310
1,1-bis-(p-chlorophenyl)-2,2,2-trichlorethane		19	82
2,4,5,4'-tetrachlorodiphenylsulphone		2000	1.2
p-chlorophenyl-p-chlorobenzene-sulphonate		2000	20

WHAT WE CLAIM IS:—

1. A pesticidal preparation which comprises a carbamate of the general formula

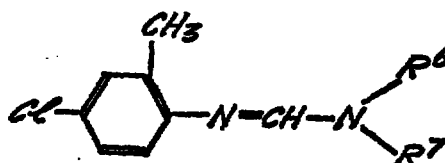


in which

R¹ represents an alkyl or cyclohexyl group,
R² and R³ each represents an alkyl group

or R²+R³ together with the adjacent nitrogen atom represent a cyclic group that may contain a further hetero atom, and

R⁴ and R⁵ each represents a hydrogen or halogen atom or an alkyl or alkenyl group, or a salt thereof, in admixture or conjunction with a formamidine of the general formula



in which

R⁶ and R⁷ each represents an alkyl group containing up to 4 carbon atoms, or R⁶ represents a hydrogen atom and R⁷ represents an alkyl group containing up to 4 carbon atoms, or a salt thereof.

2. A pesticidal preparation as claimed in claim 1, which also contains a solid or liquid carrier.

10 3. A pesticidal preparation as claimed in claim 1 or 2, which contains at least two carbamates as defined therein or salts thereof.

15 4. A pesticidal preparation as claimed in any one of claims 1 to 3, which contains at least two formamidines as defined therein or salts thereof.

20 5. A pesticidal preparation as claimed in any one of claims 1 to 4, containing 3 - dimethylaminomethyleniminophenyl - N-methylcarbamate or 4 - dimethylamino - methylenimino - 3 - methylphenyl - N - methylcarbamate or a salt thereof, in admixture or conjunction with N - (2 - methyl - 4 - chlorophenyl) - N',N' - dimethylformamidine or a salt thereof.

25 6. A pesticidal preparation as claimed in

any one of claims 1 to 5, containing the carbamate(s) and formamidine(s) in the weight ratio of from 1 to 5:1 to 10.

7. A pesticidal preparation as claimed in claim 6, containing the carbamate(s) and formamidine(s) in the weight ratio of from 1:1 to 1:2. 30

8. A pesticidal preparation as claimed in claim 1, and substantially as described in Example 1 or 2 herein. 35

9. A method of controlling pests in a crop area, wherein the crop area is treated with a preparation as claimed in any one of claims 1 to 8.

10. A method as claimed in claim 9, and conducted substantially as described in Example 1 herein. 40

11. A method of controlling pests in a commercially reared animal, wherein a preparation as claimed in any one of claims 1 to 7 is applied to a commercially reared animal. 45

ABEL & IMRAY,

Chartered Patent Agents,

Quality House, Quality Court, Chancery Lane,
London, W.C.2.

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