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PATENT SPECIFICATION

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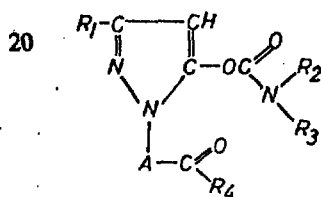
COMPLETE SPECIFICATION

New Pyrazolyl Carbamic Acid Derivatives and processes for their production

5 We, J. R. GEIGY A.G. a body corporate organised according to the laws of Switzerland of 215, Schwarzwaldallee, Basle, Switzerland, 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:—

10 The present invention concerns new heterocyclic carbamic acid esters and their salts, processes for the production thereof, pesticidal compositions containing these new compounds and their salts as active ingredients as well as processes for combatting pests by using the new compounds and/or their salts or by using compositions which contain these substances as the pesticidally active ingredients.

15 It has been found that new heterocyclic carbamic acid esters of the general formula I



wherein A represents a straight or branched chained alkylene radical which may be substituted by halogen,

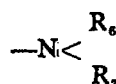
25 R₁ represents an alkyl radical with 1 to 4 carbon atoms,

R₂ represents hydrogen or a low aliphatic hydrocarbon radical,

R₃ represents a low aliphatic hydrocarbon radical,

30 R₄ represents the group —OR₅ wherein R₅ is hydrogen, an aliphatic hydrocarbon radical which may be substituted by halogen or in which the carbon chain may be interrupted by an oxygen or sulphur atom, or an alicyclic

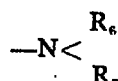
or aromatic hydrocarbon radical, or the group 35



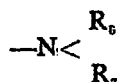
wherein R₆ and R₇ each represent hydrogen, an aliphatic or an aromatic hydrocarbon radical, or together with the adjacent nitrogen atom form a heterocyclic ring, have an excellent pesticidal activity and slight toxicity to warm blooded animals and are therefore suitable for combatting pests such as arthropodes, e.g. insects in all stages of their development as well as acarinae, e.g. spiders. They can be used, for example, as contact or systemic insecticides and are of great importance in hygiene, protection of animals and plants from attack by these pests. In addition, these compounds and their salts have a good action against fungi and bacteria. 50

By low aliphatic hydrocarbon radicals symbolised by R₂ and R₃ in general formula 1 are meant: alkyl radicals having 1 to 4 carbon atoms such as, e.g. the methyl, ethyl, propyl, isopropyl and butyl radicals and alkenyl radicals such as, e.g. the allyl, methallyl and butenyl radicals and alkynyl radicals such as, e.g. the propargyl radical. Among radicals represented by A are meant straight or branched chained alkylene radicals having 2 to 6 carbon atoms such as the ethylene, propylene, n-butylene, α-methyl-ethylene or β-propylene radicals which can be substituted by halogen atoms such as fluorine, chlorine or bromine. Substituted and unsubstituted aliphatic hydrocarbon radicals in the group —OR₅ (standing for R₅) are alkyl radicals having 1 to 7 carbon atoms such as, e.g. the methyl or ethyl radical, propyl, butyl, hexyl and heptyl radicals, alkenyl radicals having 2 to 6 carbon atoms, e.g. the allyl radical. 65 70

radical, butenyl radicals and isomers thereof, alkenyl radicals having 3 to 4 carbon atoms, e.g. the propargyl radical. These alkyl radicals and alkenyl radicals can be substituted by alkoxy groups and/or alkylthio and/or halogen atoms, particularly by chlorine or bromine. By alicyclic hydrocarbon radicals which are also represented by R_3 , are meant the cyclopentyl or cyclohexyl radical. Aromatic hydrocarbon radicals symbolised by R_3 , are, e.g. the benzyl radical, phenethyl radicals, and the cinnamyl radical. R_6 and R_7 in the group

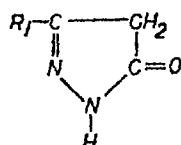


standing for R_3 in general formula 1 are independently of each other aliphatic hydrocarbon radicals which have the meanings given above for R_3 ; they are also aromatic hydrocarbon radicals such as, e.g. the phenyl radical. Among heterocyclic rings symbolised by R_3 and R_7 together with the nitrogen atom in the grouping



are meant the morpholino or piperidino radical.

The heterocyclic carbamic acid esters of the general formula 1 are obtained according to the invention by reacting at a temperature between 50° and 150°C a pyrazole derivative of general formula II:

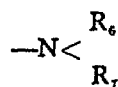


wherein R_1 represents hydrogen or a low aliphatic hydrocarbon radical with 1 to 4 carbon atoms, with a compound of general formula III:

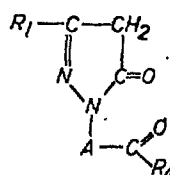


wherein Y represents a straight or branched chained, possibly halogen substituted alkenyl radical capable of forming the radical A after the addition reaction,

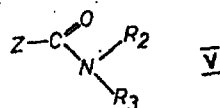
R_4 represents the group $-OR_5$, wherein R_5 is hydrogen, an aliphatic hydrocarbon radical which may be substituted by halogen or in which the carbon chain may be interrupted by an oxygen or sulphur atom, or an alicyclic or aromatic hydrocarbon radical, or the group



wherein R_6 and R_7 each represent hydrogen, an aliphatic or an aromatic hydrocarbon radical or together with the adjacent nitrogen atom form a heterocyclic ring, and reacting at a temperature between 50° and 150°C the reaction product obtained of the general formula IV:



wherein R_1 , A and R_4 have the meanings given above, with a carbamic acid halide of the general formula V:



wherein Z represents a halogen atom such as chlorine or bromine,

R_2 represents hydrogen or a low aliphatic hydrocarbon radical, and

R_3 represents a low aliphatic hydrocarbon radical.

The compounds of the general formula IV can be obtained by a variation of the process described by reacting at a temperature between 50° and 150°C, instead of a compound of the general formula III, an equivalent amount of a compound of the general formula VI:



wherein Y has the meaning given (under formula III), with a compound of general formula II, and the converting the reaction product obtained into a compound of the general formula IV by saponification and/or esterification in the presence of an inorganic acid. The imido esters formed as intermediate products on esterifying in the presence of an inorganic acid can be isolated in the form of their salts and, if desired, reacted with an amine to form amidines. The compounds of the general formula IV b can be obtained from these amides.

The compounds of the general formula IV can also be produced by condensing hydrazine or derivatives thereof with a cyanide of the general formula VI, then condensing with a β -ketocarboxylic acid ester or diketene and

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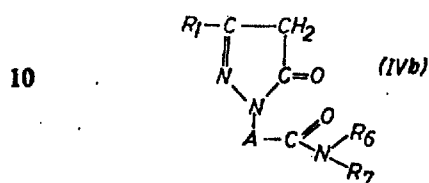
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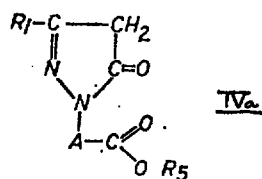
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- 5 saponifying and/or esterifying the cyano group. Also, a good yield of the compounds of general formula IV are obtained from the reaction of hydrazine or derivatives thereof with a compound of the general formula III and subsequent condensation with a β -keto acid ester or diketene.

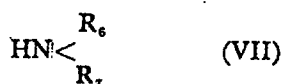
The compounds of the general formula IV b:



wherein A, R₁, R₆ and R₇ have the meanings given above, are obtained if a compound of the general formula IV a:



- 15 wherein R₁ and A have the meanings given above,
 R₅ represents hydrogen or an aliphatic, alicyclic or aromatic hydrocarbon radical which may be substituted, is reacted at a temperature between 50° and 150°C under pressure with an amine of general formula VII:



- wherein R₆ and R₇ have the meaning given above.
- 25 According to another variation of the process described, a pyrazole derivative of general formula II is reacted at a temperature between 50° and 150°C with a compound of general formula V to form the corresponding carbamic acid ester and then with a compound of the general formula III.
- 30 If desired, the reaction products of the general formula I are afterwards converted into their salts by reaction with organic or inorganic acids.
- 35 The two-step process and its variations described above are performed, if necessary, in the presence of organic solvents such as, e.g. aromatic hydrocarbons, ketones, esters and amides. The reaction of the pyrazole derivatives of the general formula II or of the carbamic acid esters produced therefrom with compounds of the general formula III is per-

formed, if necessary, in the presence of a cationic or anionic catalyst such as, e.g. glacial acetic acid, potassium carbonate, trimethylamine, triethylamine and pyridine. The temperatures at which the reactions in the two-step process and the variations thereof are performed are preferably between 80 and 120°C.; the duration may be 8 to 24 hours.

The reactions with compounds of general formula V are preferably performed in the presence of an organic or inorganic base or in the presence of a solvent. Examples of organic bases are tertiary amines such as triethylamine and pyridine, examples of inorganic bases are potassium carbonate and hydroxides of alkali and alkaline earth metals. Solvents which can be used are, e.g. aromatic hydrocarbons as well as ketones, esters and amides.

In another method of performing the process, phosgene and the corresponding alkylamines are used instead of compounds of general formula V. To produce compounds of general formula I wherein R₂ is hydrocarbon, according to another variation, the compounds of general formula II are reacted with an alkyl isocyanate. In this variation of the process also, the reactions can be performed in the presence of the solvents and organic or inorganic bases mentioned above.

In the process and variations thereof described, the esters and amides of the following alkenyl carboxylic acids can be used as compounds of general formula III: acrylic acid, α - methylacrylic acid, crotonic acid, β - ethylacrylic acid, β - propylacrylic acid, α - methyl - β - ethylacrylic acid, α, β - dimethylacrylic acid, β, β - dimethylacrylic acid, trimethylacrylic acid, allylacetic acid, hydro-sorbic acid, dimethylvinyl acetic acid, α -ethylcrotonic acid, α -chlorocrotonic acid, β -bromocrotonic acid, γ, γ, γ - trichlorocrotonic acid.

Acrylonitrile and the cyanides corresponding to the alkenyl carboxylic acids given above can be used for example as alkenyl cyanides of general formula VI.

Compounds of the following types, for example, are produced by the method described above and the variations thereof:

- 1 - [α - alkyl - β - (alkoxycarbonyl) - ethyl] - 3 - alkyl - pyrazolyl - (5) - carbamic acid ester, 95
- 1 - [β - alkyl - β - (alkoxycarbonyl) - ethyl] - 3 - alkyl - pyrazolyl - (5) - carbamic acid ester, 95
- 1 - [α - halogen - β - (alkoxycarbonyl) - ethyl] - 3 - alkyl - pyrazolyl - (5) - carbamic acid ester, 100
- 1 - [α - alkyl - β - (alkylcarbonyl) - ethyl] - 3 - alkyl - pyrazolyl - (5) - carbamic acid ester, 105
- 1 - [β - alkyl - β - (dialkylcarbonyl) - ethyl] - 3 - alkyl - pyrazolyl - (5) - carbamic acid ester,

1 - [β - (alkoxycarbonyl) - ethyl] - 3 - alkyl-pyrazolyl - (5) - carbamic acid ester.

5 The compounds of the general formula I are also stable in water, dissolve well in organic solvents and sometimes also in water. In general, they are liquids which can be distilled well; some are crystalline with a low melting point.

10 The compounds of general formula I have been tested for their activity against insects of the following orders or types:

	Heteroptera:	Pyrrhocoridae
	Homoptera:	Pseudococcidae
		Aphididae
15	Diptera:	Culicidae
		Muscidae
	Orthoptera:	Acrididae
		Blattidae
20	Coleoptera:	Dermestidae
		Tenebrionidae
		Chrysomelidae
		Bruchidae
		Curculionidae
25	Lepidoptera:	Pyalididae
		Noctuidae
	Hymenoptera:	Formicidae

as well as spiders of the families: Tetranychidae, Argasidae and Ixodidae of the Acarina order.

30 The results showed that the compounds have a good to very good contact and stomach poisoning action combined with a very clear systemic action. They thus have a particularly wide range of action.

35 It was found that the compounds of general formula I have an excellent action against insects of the families Muscidae and Culicidae, for example, the polyvalent resistant and normal sensitive house flies (*Musca domestica*) and mosquitoes (*Aedes aegyptii*, *Culex fatigans*, *Anopheles staphensi*), of the families

Curculionidae, Bruchidae, Dermestidae, Tenebrionidae, Chrysomelidae, for example, granary weevils (*Sitophilus granaria*), bean weevils (*Bruchidius obtectus*), hide beetles (*Dermestes vulpinus*), yellow mealworms (*Tenebrio molitor*), Colorado potato beetles (*Leptinotarsus decemlineata*) and their larvae in all stages of development of the family Calophoridae (*Lucilia cuprina*) and their larvae of the families Pyralididae, e.g. Mediterranean flour moth larvae (*Ephestia kühniella*), Blattidae, e.g. German cockroaches (*Phyllodromia germanica*), Aphididae, e.g. bean aphids (*Aphis fabae*) and Pseudococcidae, e.g. citrus mealy bugs (*Phanococcus citri*).

Tests made with leaf aphids (*Aphis fabae*) and desert locusts (*Schistocerca gregaria*) indicate an excellent systemic action in plants. Thus the compounds of the general formula I can be used as plant protection insecticides just as well as hygiene and veterinary insecticides.

In order to determine the insecticidal activity of compounds according to the invention, the formulas of which are given in the 1st column of Table III below, these compounds were applied to the surface of aluminium foils on the one hand and wooden boards on the other hand in concentration of 1g/sq. meter. The objects having surfaces thus prepared were stored at room temperature (20°C) 28 and 60 days, respectively, after the time of applying the active substance, glass bells were placed with their opening upon the aforesaid surfaces. Each glass bell contained 10 mosquitoes (*Aedes Aegypti*) or 10 cockroaches (*Phyllodromia germanica*) respectively. The time is determined within which all insects have adopted dorsal position. These times are given in the 2nd and 3rd column of Table III for mosquitoes and in the 4th and 5th column of Table III for cockroaches.

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TABLE III

Test compound	All test insects in dorsal position			
	mosquitoes		cockroaches	
	28 days	60 days	28 days	60 days
$ \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_4\text{COOC}_2\text{H}_5 \end{array} \text{OCON}(\text{CH}_3)_2 $	14	15	35	35
$ \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_4\text{COO}-n\text{C}_3\text{H}_7 \end{array} \text{OCON}(\text{CH}_3)_2 $	15	15	35	40
$ \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_4\text{COOCH}_2-\text{CH}=\text{CH}_2 \end{array} \text{OCON}(\text{CH}_3)_2 $	14	17	35	45
$ \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_4\text{CON}(\text{CH}_3)_2 \end{array} \text{OCON}(\text{CH}_3)_2 $	10	15	95	90

5 Spotted spider mites (*Tetranychus urticae*) were used to test the acaricidal activity of compounds of the general formula I. It was found that they had a very good action, particularly against the adults and larval stages.

In order to determine the acaricidal activity of the test compounds, the formulas of which are shown in the 1st column of Table IV

below, bean leaves (*Vicia faba*) infested with adults and larval of red spiders (*Tetranychus urticae*) are sprayed with an 0.1% aqueous emulsion or solution of the test compounds. After 3 days the % of killed animals of both the adult and the larval stage is determined. The determined data are given in the 2nd column of Table IV. 10 15

TABLE IV

5	iodi chlo are prec conc disti 3 - carb 152-
10	10 N - acry of g in a 15 ture of e 10% water 20 sodi the carb (5) - It b 25 sure O ponc pou in th 30 1 - 3 ca 1 - m 35 ca 1 - m ca 40 1 - m ca 1 - m ca 45 1 - m ca 1 - m ca 50 1 - m ca 15 55 1 - m ca 1 - m 60 1 - 3 ca

48 Parts of 1 - [β - (methoxycarbonyl) - ethyl] - 3 - methyl - pyrazolone - (5), 44 parts of calcined potash, 0.5 parts of potassium

iodide and 31 parts of dimethylcarbamic acid chloride in 400 parts by volume of benzene are refluxed for 15 hours while stirring. The precipitate is filtered off and the filtrate is concentrated in vacuo. The residue can be distilled. 1 - [β - (methoxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester is obtained. B.P._{0.01}: 152—156°.

EXAMPLE 2

16.9 Parts of 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, 10 parts of acrylic acid ethyl ester and 3 parts by volume of glacial acetic acid are heated at 100—105° in an oil bath for 15 hours. The reaction mixture is then diluted with 150 parts by volume of ether, the ethereal solution is washed with 10% sodium carbonate solution and then with water and the ethereal solution is dried with sodium sulphate. After removal of the ether, the residue is distilled. 1 - [β - (ethoxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - dimethylcarbamic acid ester is obtained. It boils at 170—171.5° under 0.03 mm pressure.

On using equivalent amounts of the corresponding acrylic acid ester, the following compounds are obtained by the method described in the above examples:

- 30 1 - [β - (β' - chloroethoxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.03}: 190—196.5°.
- 35 1 - [β - (propoxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.01}: 164—165°.
- 40 1 - [β - (isopropoxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.02}: 152—153°.
- 45 1 - [β - (allyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.02}: 176—178°.
- 50 1 - [β - (n - butyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.006}: 135—136°.
- 55 1 - [β - (isobutyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.005}: 145—150°.
- 60 1 - [β - (sec. butyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.001}: 156°.
- 1 - [β - (n - amyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.001}: 149.5—151.5°.
- 1 - [β - (isoamyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.0025}: 177—178°.
- 1 - [β - (n - hexyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.02}: 163°.
- 1 - [β - (cyclohexyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.02}: 200—205°.

- 1 - [β - (cyclopentyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.04}: 153—154°.
- 1 - [β - (β' - methoxyethoxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester, B.P._{0.001}: 152—154°.
- 1 - [β - (N - n - propylcarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester MP.: 72—75°.
- 1 - [β - (N - di - n - propylcarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.4}: 170—175°.
- 1 - [β - (ethyloxycarbonyl) - propyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.0025}: 146—150°.
- 1 - [β - (N - di - ethylcarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.01}: 167—170.5°.
- 1 - [β - (N - di - isopropylcarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.005}: 145—146°.
- 1 - [β - (N - n - butylcarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.03}: 169—174°.
- 1 - [α - methyl - β - (ethyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.003}: 140°.
- 1 - [β - (N - phenylcarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester M.P.: 143—144.5°.
- 1 - [β - (methyloxycarbonyl) - propyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.015}: 151°.
- 1 - [β - (β' - methylthio) - ethyloxycarbonyl - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethylcarbamic acid ester B.P._{0.008}: 180—186°.
- 1 - [β - (ethyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - diethylcarbamic ester B.P._{0.06}: 153—156°.
- 1 - [β - (ethyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - diallylcarbamic acid ester B.P._{0.05}: 160—162°.

EXAMPLE 3

37 Parts of 1 - (β - methoxycarbonyl)ethyl - 3 - methyl - pyrazolone - (5), 110 parts of a 41% aqueous dimethylamine solution and 110 parts by volume of ethanol are rotated in a steel autoclave for 8 hours at 80—100°. To work up, animal charcoal is added to the dark solution which is then filtered. The filtrate is concentrated in vacuo. The residue is extracted 4 times with 100 parts of hot benzene to remove non-reacted carboxyl esters. The undissolved residue is further worked up. 38 Parts of the residue, 53.1 parts of calcined potassium carbonate, 2 parts of potassium iodide, 50.2 parts of dimethylcarbamic acid chloride in 150 parts by volume of benzene are refluxed for 12 hours while stirring. The precipitate formed is filtered off and the benzene is distilled off in vacuo. The residue, 1 - [β - (N - dimethylcarbonyl) - ethyl] -

3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester is purified by distillation. B.P. _{0.01} : 152—153.5°.

- 5 Using an equivalent amount of 35% aqueous methylamine solution in the method described above, 1 - [β - (methylcarbamy)] - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester is obtained. It melts at 85—88°.

10 EXAMPLE 4

- 49 Parts of 3 - methylpyrazolone - (5) are suspended in 300 parts by volume of dimethyl formamide. 2 Parts by volume of glacial acetic acid are then added and 27 parts of acrylonitrile are added dropwise at room temperature. The reaction mixture is then stirred for 12 hours at 80° whereupon a clear solution is formed. This solution is worked up by evaporating off the solvent and recrystallising the residue from benzene. 1 - [β - cyanoethyl] - 3 - methyl - pyrazolone - (5) is obtained. M.P. 111—112.5°.

- 62 Parts of 1 - [β - cyanoethyl] - 3 - methyl - pyrazolone - (5) are refluxed for 5 hours with 300 parts by volume of concentrated hydrochloric acid. The reaction mixture is worked up by neutralising to a pH of 7 while cooling with ice and then evaporating to dryness in a rotary evaporator. The residue is purified by recrystallisation from water. The acid melts at 178—180°.

- 17 Parts of the above acid are esterified by dissolving in 250 parts by volume of methanol and adding 1 part by volume of concentrated sulphuric acid. The solution is refluxed for 12 hours, whereupon it is worked up by evaporating to dryness and recrystallising the residue from water. 1 - [β - (methoxycarbonyl) - ethyl] - 3 - methyl - pyrazolone - (5) is obtained (M.P. 105—112°). This can be worked up and converted into 1 - [β - (N - dimethylcarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester as described in example 3.

- As has already been mentioned, the compounds according to the present invention have an extraordinarily wide range of action and can be used for the combatting of pests in the most various fields. Because of the many types of pests which can be combatted, the various forms of application must, therefore, be adapted to the special purposes desired. It is recommended and also more economical, to combine the active ingredients with suitable additives, including water; solutions, dispersions, pastes, dusts and sprinkling agents and wettable powders are particularly suitable forms for application. The dispersions, pastes and wettable powders (for spraying) are concentrates which can be diluted with water, so forming suspensions and emulsions, to any concentration desired.

Organic solvents such as aliphatic and alicyclic alcohols, ketones, hydrocarbons such as

benzene, xylenes, toluene, benzines, also chlorinated and fluorinated hydrocarbons as well as water are used in particular for the production of solutions. In some cases it is necessary to produce a so-called carrier solution from the active ingredient and the solvents mentioned above and then to dissolve this in higher boiling solvents, e.g. in petroleum fractions such as kerosene, methyl naphthalenes, xylenes, benzines etc. Solutions of active substances in aromatic hydrocarbons such as, e.g. xylenes, toluene and halogenated hydrocarbons such as chlorobenzene and such like are particularly suitable for direct spraying of objects and for the impregnation of materials such as, e.g. textiles.

In addition to the form of organic solutions, the active substances according to the invention can also be applied in aqueous forms such as dispersions (emulsions and suspensions). To produce an emulsion, the substances, in one of the solvents mentioned above, are homogenised in water, preferably in the presence of a dispersing agent.

Cationic, anionic and non-ionogenic preparations are employed as dispersing or emulsifying agents. Examples of cationic preparations which can be used are quaternary ammonium compounds and morpholine derivatives. Anionic dispersing or emulsifying agents are soaps, alkali and alkaline earth salts of long chained aliphatic sulphuric acid monoesters, of aliphatic-aromatic sulphonic acids or of long chained alkoxyacetic acids. Examples of non-ionogenic dispersing or emulsifying agents which can be used to work up the active substances according to the invention into pest control agents are polyethylene glycol ethers of fatty alcohols or alkylphenols, polycondensation products of ethylene and propylene oxides, water soluble cellulose derivatives, alkyl alkanolamides and sugar derivatives of higher fatty acids. Also, film-forming and adhesive agents can be added to the emulsions or dispersions such as, e.g. mineral and vegetable oils, polyvinyl alcohols, polyvinyl pyrrolidones or hydroxyalkyl cellulose. Also, paste-like or liquid concentrates can be produced from the active substances according to the invention and the emulsifying and dispersing agents mentioned above, possibly with the addition of solvents, thickeners, protective colloids and other ointment bases, which concentrates can be diluted with water to any concentration desired.

For dusts and sprinkling agents, the active ingredients are brought onto finely milled or granulated carriers by various means. The carriers can be inert, acid or alkaline. Thus, the carriers can be impregnated with the solutions of the active substances as described above, also the solid active substances can be milled with the carriers or the carriers can be impregnated with the melted active substances. Carriers for these forms for applica-

tion are inorganic silicates, e.g. kaolines, montmorillonites, bentonites, zeoliths, kieselguhr, diatomaceous earth, powdered glass, loess, also talcum, magnesia usta, boric acid, tricalcium phosphate, in some cases calcium carbonate, for example in the form of whiting, burnt lime and finely ground limestone. In addition organic substances such as sawdust, powdered cork, walnut shell flour or walnut shell granulate etc. can serve as carriers. Also, it is advisable to use mixtures of the inorganic and/or organic carriers mentioned above.

Pulverulent preparations can be made suspendible in water by the addition of capillary active substances such as wetting agents, e.g. sulphite waste liquor, and dispersing agents e.g. those mentioned above, and in the suspended form can be used as wettable powders. In some cases the addition of adhesives such as, e.g. polyvinyl alcohols, polyvinyl pyrrolidone, alkaline earth salts and alkali metal salts of long chained, aliphatic fatty acids, mineral or vegetable oils as well as certain protective colloids and/or thickeners such as glue, alginates and casein is recommended.

The following examples describe the production of various forms for application. The parts are given as parts by weight.

EXAMPLE I

Spray:

a) 2 Parts of 1 - [β - (ethyloxycarbonyl)-ethyl] - 3 - methylpyrazolyl - (5) - N - dimethyl - carbamic acid ester are dissolved in 10 parts of xylene and 88 parts of petroleum.

b) 2 Parts of the same active substance and 3 parts of 1,1 - bis - (p - chlorophenyl) - 2,2,2 - trichloroethane are dissolved in 10 parts of xylene or another auxiliary solvent and 85 parts of petroleum.

Both solutions are excellently suitable, for example for combatting flies and mosquitoes in houses as well as in store rooms and slaughter houses.

EXAMPLE II

Smoke

a) 20 Parts of 1 - [β - (allyloxycarbonyl)-ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl - carbamic acid ester are mixed with 61 parts of sawdust which has been previously impregnated with 18.4 parts of potassium nitrite, and the mass is made, under pressure, into tablets.

b) 50 Parts of the same active substance, 22 parts of sugar, 12 parts of potassium chlorate, 2.4 parts of potassium nitrate and 13.6 parts of sawdust are milled and thoroughly mixed. The mass is put into boxes and lit with a wick or fuse.

EXAMPLE III

Smoke Papers

Ordinary filter paper is treated with a 5% potassium nitrate solution. The 1 - [β - (8'-methoxyethyl - carbonyl) - ethyl] - 3 - methylpyrazolyl - (5) - N - dimethyl - carbamic acid ester is drawn onto this filter paper in the form of a 25% acetone solution. The smoke paper so obtained contains about 30% of active substance.

The insecticidal smoke formed from the tablets and the mass for smoking is especially suitable for combatting insects in enclosed spaces.

EXAMPLE IV

Vapour

1 - [β - (propyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester as such or with suitable additives which promote evaporation, is evaporated by heating, e.g. on an electric hot plate. In this way, the insects in an enclosed space are killed.

EXAMPLE V

Dust

1 Part 1 - [β - (methyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester is milled as finely as possible with 99 parts of talcum. The adhesive power of this powder can be increased by the addition of 2 parts of a liquid fatty acid. This dust can be used, for example, for combatting pests particularly in the household and in larders and storerooms.

EXAMPLE VI

Sprinkling Agent

1 Part 1 - [β - (N - dimethylcarbonyl)-ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester is mixed with 99 parts of a silicate. This sprinkling agent is suitable for all uses where a finely pulverised material is unsuitable because of dust formation.

EXAMPLE VII

Emulsion

25 Parts 1 - [β - (N - n - butylcarbonyl)-ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester are dissolved in a mixture of 50 parts of cyclohexanone and 15 parts of dimethyl formamide and 10 parts of a mixture of an alkylaryl ethylene condensation product and of an alkylaryl sulphonic acid salt are added. This concentrate can be diluted with water to any concentration desired to form an emulsion.

EXAMPLE VIII

Wettable powder

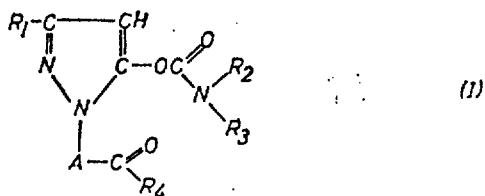
a) 25 Parts 1 - [β - (ethyloxycarbonyl)-ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester 15 parts of a silicate, e.g. a celite, 52.5 parts of kaolin, 5

parts of a wetting agent such as, e.g. a sulphuric acid ester of an alkyl polyglycol ether and 2.5 parts of a dispersing agent, e.g. a polyvinyl pyrrolidone or a neutralised condensation product of naphthalene sulphonic acids and formaldehyde, are thoroughly mixed and milled. An about 25% wettable powder is obtained, with which stable suspensions can be produced with water in the presence of an additive which regulates the pH value. The total suspension power of this form for application is 87%; it can be well wetted and pasted.

b) 25 Parts of the same active substance are mixed and milled with 10 parts of a silicate, 5 parts of a dispersing agent, for example, an alkylpolyglycol ether, 2 parts of a wetting agent, e.g. an ethylene oxide condensation product, and about 50 parts of kaolin.

WHAT WE CLAIM IS:—

1. New heterocyclic carbamic acid esters of the general formula 1:



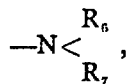
wherein A represents a straight or branched chained alkylene radical which may be substituted by halogen,

R₁ represents an alkyl radical with from 1 to 4 carbon atoms,

R₂ represents hydrogen or a low aliphatic hydrocarbon radical,

R₃ represents a low aliphatic hydrocarbon radical,

R₄ represents the group —OR₅ wherein R₅ represents hydrogen, an aliphatic hydrocarbon radical which may be substituted by halogen or in which the carbon chain may be interrupted by an oxygen or sulphur atom, or an alicyclic or aromatic hydrocarbon radical, or the group



wherein R₆ and R₇ each represent hydrogen, an aliphatic or aromatic hydrocarbon radical or together with the adjacent nitrogen atom form a heterocyclic ring as well as their salts with organic or inorganic acids.

2. 1 - [β - (ethyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

3. 1 - [β - (propyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

4. 1 - [β - (methyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

5. 1 - [β - (allyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

6. 1 - [α - methyl - β - (ethyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

7. A pesticidal composition which comprises at least one pesticidally active heterocyclic carbamic acid ester of the general formula I as defined in claim 1 in admixture with a suitable carrier and/or distributing agent.

8. A pesticidal composition which comprises at least one salt of a heterocyclic carbamic acid ester of the general formula I as defined in claim 1.

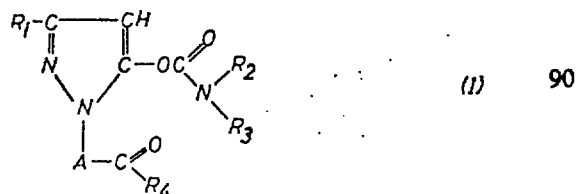
9. A method of combatting pests in a selected area which comprises disposing in said area at least one compound of the general formula I as defined in claim 1.

10. A method for combatting pests, which comprises contacting said pests with at least one compound of the general formula I as defined in claim 1 or with a salt of such compound.

11. A method of combatting pests in a selected zone which comprises disposing in said zone a composition as claimed in claim 7 or 8.

12. A method of combatting pests which comprises contacting said pests with a composition as claimed in claim 8 or 9.

13. Process for the production of a heterocyclic carbamic acid ester of the general formula 1



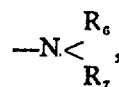
wherein A represents a straight or branched chained alkylene radical which may be substituted by halogen,

R₁ represents an alkyl radical with from 1 to 4 carbon atoms,

R₂ represents hydrogen or a low aliphatic hydrocarbon radical,

R₃ represents a low aliphatic hydrocarbon radical,

R₄ represents the group —OR₅ wherein R₅ is hydrogen, an aliphatic hydrocarbon radical which may be substituted by halogen or in which the carbon chain may be interrupted by an oxygen or sulphur atom or an alicyclic or aromatic hydrocarbon radical or the group



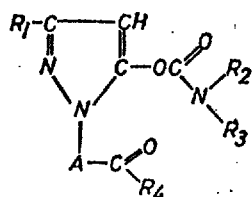


parts of a wetting agent such as, e.g. a sulphuric acid ester of an alkyl polyglycol ether and 2.5 parts of a dispersing agent, e.g. a polyvinyl pyrrolidone or a neutralised condensation product of naphthalene sulphonic acids and formaldehyde, are thoroughly mixed and milled. An about 25% wettable powder is obtained, with which stable suspensions can be produced with water in the presence of an additive which regulates the pH value. The total suspension power of this form for application is 87%; it can be well wetted and pasted.

b) 25 Parts of the same active substance are mixed and milled with 10 parts of a silicate, 5 parts of a dispersing agent, for example, an alkylpolyglycol ether, 2 parts of a wetting agent, e.g. an ethylene oxide condensation product, and about 50 parts of kaolin.

WHAT WE CLAIM IS:—

1. New heterocyclic carbamic acid esters of the general formula 1:



(I)

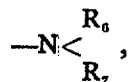
wherein A represents a straight or branched chained alkylene radical which may be substituted by halogen,

R₁ represents an alkyl radical with from 1 to 4 carbon atoms,

R₂ represents hydrogen or a low aliphatic hydrocarbon radical,

R₃ represents a low aliphatic hydrocarbon radical,

R₄ represents the group —OR₅, wherein R₅ represents hydrogen, an aliphatic hydrocarbon radical which may be substituted by halogen or in which the carbon chain may be interrupted by an oxygen or sulphur atom, or an alicyclic or aromatic hydrocarbon radical, or the group



wherein R₆ and R₇ each represent hydrogen, an aliphatic or aromatic hydrocarbon radical or together with the adjacent nitrogen atom form a heterocyclic ring as well as their salts with organic or inorganic acids.

2. 1 - [β - (ethyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

3. 1 - [β - (propyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

4. 1 - [β - (methyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

5. 1 - [β - (allyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

6. 1 - [α - methyl - β - (ethyloxycarbonyl) - ethyl] - 3 - methyl - pyrazolyl - (5) - N - dimethyl carbamic acid ester.

7. A pesticidal composition which comprises at least one pesticidally active heterocyclic carbamic acid ester of the general formula I as defined in claim 1 in admixture with a suitable carrier and/or distributing agent.

8. A pesticidal composition which comprises at least one salt of a heterocyclic carbamic acid ester of the general formula I as defined in claim 1.

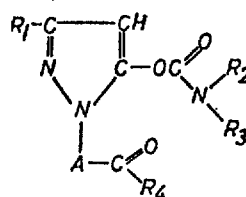
9. A method of combatting pests in a selected area which comprises disposing in said area at least one compound of the general formula I as defined in claim 1.

10. A method for combatting pests, which comprises contacting said pests with at least one compound of the general formula I as defined in claim 1 or with a salt of such compound.

11. A method of combatting pests in a selected zone which comprises disposing in said zone a composition as claimed in claim 7 or 8.

12. A method of combatting pests which comprises contacting said pests with a composition as claimed in claim 8 or 9.

13. Process for the production of a heterocyclic carbamic acid ester of the general formula 1



(II)

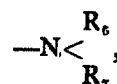
wherein A represents a straight or branched chained alkylene radical which may be substituted by halogen,

R₁ represents an alkyl radical with from 1 to 4 carbon atoms,

R₂ represents hydrogen or a low aliphatic hydrocarbon radical,

R₃ represents a low aliphatic hydrocarbon radical,

R₄ represents the group —OR₅, wherein R₅ is hydrogen, an aliphatic hydrocarbon radical which may be substituted by halogen or in which the carbon chain may be interrupted by an oxygen or sulphur atom or an alicyclic or aromatic hydrocarbon radical or the group



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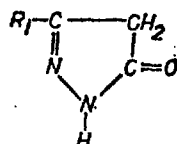
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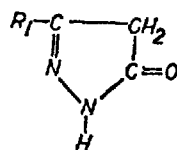
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- 5 wherein R_1 and R_2 each represent hydrogen, an aliphatic or aromatic hydrocarbon radical, or together with the adjacent nitrogen atom form a heterocycle ring, which comprises reacting at a temperature between 50° and 150°C a pyrazole derivative of the general formula 11:

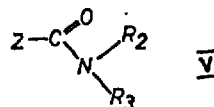


(II)



(II)

wherein R_1 has the meaning given in claim 13, with the carbamic acid halide of general formula V

V

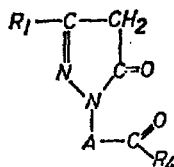
- 10 wherein R_1 has the meaning given above, with a compound of the general formula 111



(III)

wherein Z, R_2 and R_3 have the meanings given in claim 13, and then reacting at a temperature between 50° and 150°C the reaction product obtained with the compound of the general formula III:

- 15 wherein Y represents a straight or branched chained, possibly halogenated alkenyl radical capable of forming the radical A after the addition reaction, and
 R_4 has the meaning given above, and reacting at a temperature between 50° and 150°C the reaction product obtained of the general formula IV



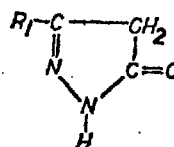
(IV)



(III)

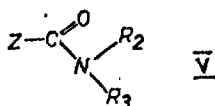
wherein Y and R_4 have the meanings given in claim 13, and if desired, converting the product obtained into a salt.

15. Modification of the process as claimed in claim 13, which comprises reacting at a temperature between 50° and 150°C a pyrazole derivative of the general formula II

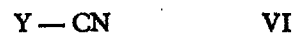


(II)

wherein R_1 , A and R_4 have the meanings given above, with a carbamic acid halide of the general formula V:

V

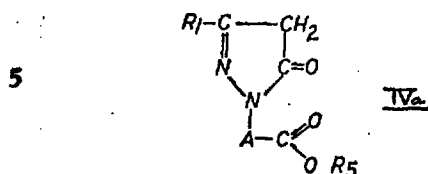
wherein R_1 has the meaning given in claim 13 with an equivalent amount of a compound of the general formula VI



wherein Y has the meaning given in claim 13, and converting the reaction product so obtained by saponification and/or esterification in the presence of an inorganic acid, into a compound of the general formula IV defined in claim 10 and reacting at a temperature between 50° and 150°C said compound with a carbamic acid halide of the general formula V defined in claim 13, and if desired converting the product obtained into a salt.



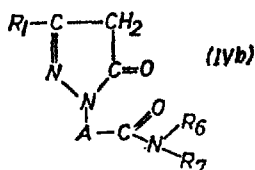
16. Modification of the process claimed in claim 13, which comprises reacting at a temperature between 50° and 150°C under pressure a compound of formula IV a:



wherein R₁, R₅ and A have the meanings given in claim 13, with an amine of the general formula VII:



10 wherein R₆ and R₇ have the meanings given in claim 13, then reacting at a temperature between 50° and 150°C the pyrazole derivative so obtained of the general formula IV b:



15 with a carbamic acid halide of the general formula V defined in claim 13, and, if desired, converting the reaction products into their salts.

20 17. Modification of the process as claimed in claims 13 or 14, which comprises using phosgene and an amine of the general formula



25 wherein R₂ and R₃ have the meanings given in claim 13, instead of a compound of the general formula V.

30 18. Process as claimed in claim 13 or 14 which comprises performing the reaction with an alkyl isocyanate instead of a carbamic acid halide of the general formula V defined in claim 13.

19. Process as claimed in any of claims 13 to 18 in which the reactions are performed in the presence of an organic solvent.

20. Process as claimed in claim 19 in which said organic solvent comprises an aromatic hydrocarbon, a ketone, an ester or an amide.

21. Process as claimed in any of claims 13 to 20 in which the reaction of a compound of the general formula II as defined in claim 13 or a carbamic acid ester produced therefrom, with a compound of the general formula III as defined in claim 13 is carried out in the presence of an anionic or cationic catalyst.

22. Process as claimed in claim 21 in which said catalyst comprises glacial acetic acid, potassium carbonate, trimethylamine, triethylamine or pyridine.

23. Process as claimed in any of claims 13 to 22 in which the reactions are performed at a temperature of from 50 to 150°C.

24. Process as claimed in claim 23 in which the reactions are performed at a temperature of from 80 to 120°C.

25. Process as claimed in any of claims 13 to 24 in which the duration of the reactions is from 8 to 24 hours.

26. New heterocyclic carbamic acid esters of the general formula I as defined in claim 1 substantially as hereinbefore described with reference to and as illustrated in any of Examples 1 to 3.

27. New heterocyclic carbamic acid esters of the general formula I as defined in claim 1 substantially as hereinbefore described with reference to and as illustrated in Example 4.

28. Process for the production of new carbamic acid esters of the general formula I as defined in claim 1 substantially as hereinbefore described with reference to and as illustrated in any of Examples 1 to 3.

29. Process for the production of new carbamic acid esters of the general formula I as defined in claim 1 substantially as hereinbefore described with reference to and as illustrated in Example 4.

30. A pesticidal composition as claimed in claim 7 substantially as hereinbefore described in any of the Examples 1 to VIII.

31. A method of combatting pests substantially as hereinbefore described.

32. A method of combatting pests in a selected zone which comprises disposing in said selected zone a composition substantially as hereinbefore described with reference to and as illustrated in any of Examples I to VIII.

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