

PATENT SPECIFICATION

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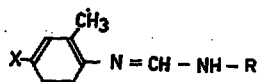


(54) METHOD OF COMBATING PADDY STEM BORERS USING SUBSTITUTED PHENYL AMIDINES

(71) We, CIBA-GEIGY AG, a body corporate organised according to the laws of Switzerland, of 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:—

This invention relates to a method of combating paddy stem borers using substituted phenylamidines.

According to the present invention, there is provided a method of combating paddy stem borers which comprises treating said paddy stem borers or their locus or habitat with a compound of the formula I:



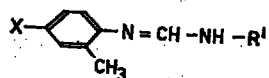
(I)

wherein

R represents an alkyl group containing maximally 4 carbon atoms, and
 X represents a fluorine, chlorine, bromine or iodine atom,
 or with a salt of such a compound with an inorganic acid.

The alkyl group R may be branched or unbranched.

Preferred compounds used in the invention are those of the formula:



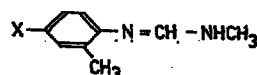
(II)

in which R' represents an unbranched C₁—C₄

[Price 25p]

alkyl group and X has the meaning given above.

Compounds of the formula:



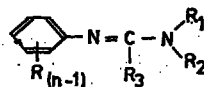
(III)

in which X has the meaning given above, are particularly valuable. X represents a fluorine, bromine or iodine atom, for example a bromine atom; or X represents a chlorine atom.

The compounds of the formula I may be used as free bases or in the form of their salts with inorganic acids, especially hydrochloric acid.

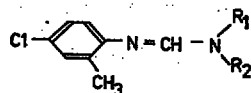
The compounds of the formula I are manufactured according to methods which are in themselves known. Appropriately, the procedure to be followed is that monoalkyl-amine, formylated at the nitrogen atom, is reacted with equivalent amounts of phosphorus oxychloride, optionally in an organic solvent at 20° C to 100° C, and subsequently with an equivalent amount of 2-amino-5-halogenotoluene. Another possibility consists in manufacturing the corresponding imino ester in the usual way and then converting it with monoalkyl-amine into the formamidine.

British Patent No. 964640 discloses that compounds of the formula

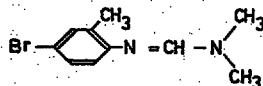


in which R represents a halogen atom, a C₁ to C₄ alkyl, alkoxy, halogenoalkyl radical or

- a phenoxy radical substituted by one or more halogen atoms, a C_1 to C_4 alkyl, alkoxy, or halogenoalkyl radical or represents the group $-CF_3$, $-NO_2$, $-CN$, $-SCN$, n stands for the numbers 1 to 4, R_1 represents an alkyl radical containing 1 to 3 carbon atoms, R_2 and R_3 each stands for hydrogen or a C_1 to C_4 alkyl group, and the radicals R_1 and R_2 together with the nitrogen atom may also be constituents of a heterocyclic ring, or the salts of these compounds, can be used as active substances in pesticidal agents. The activity spectrum of these compounds has been defined very broadly and relates to the herbicidal insecticidal, acaricidal and nematocidal field.
- British Patent No. 1039930 discloses that the compounds of the formula



- in which R_1 stands for hydrogen or alkyl containing up to 4 carbon atoms and R_2 stands for alkyl containing up to 4 carbon atoms, or the salts thereof, possess in particular acaricidal-ovicidal activity.
- British Patent No. 1122580 discloses that the compound of the formula



- exhibits in particular acaricidal activity.
- It has now been surprisingly discovered that the compounds of the formula I, besides having a general acaricidal activity, are distinguished by particularly strong activity against paddy stem borers.
- The paddy stem borers to be combated according to the invention include, for example, *Chilo suppressalis*, *Chilo diffusilinea*, *Chilo portellus*, *Chilorea auricilia*, *Chilorea polychrysa*, *Tryporyza incertulas*, *Tryporyza innotata*, *Sesamia inferens*, *Sesamia cretica* and *Sesamia calamistis*. In addition to their destructive action, the compounds of the formula I also possess an anti-feeding effect. Their systematic effect is particularly advantageous.
- The active substances of the formula I may be used by themselves or together with suitable carriers and/or adjuvants. Suitable carriers and adjuvants are solid or liquid and correspond to the substances conventionally used in formulation technique; for example, natural or regenerated substances, solvents, dispersants, wetting agents, adhesives, thickeners, binders and/or fertilisers. It is also possible

to add still further compounds which possess insecticidal or acaricidal activity.

Such biocidal compounds may belong, for example, to the class of the ureas, the saturated and unsaturated halogeno fatty acids, halogenated hydrocarbons, carbamates, triazines, nitroalkyl phenols, organic phosphoric acid compounds, quaternary ammonium salts, sulphamic acids, arsenates, arsenites, borates or chlorates.

For application purposes the compounds of the formula (I) may be processed to dusts, emulsion concentrates, granules, dispersions, sprays, to solutions or suspensions of the conventional formulation which is universally known in application technology.

In order to manufacture solutions of the compounds of the formula (I) which may be directly sprayed, it is possible to use, for example, mineral oil fractions of high to medium boiling range, such as diesel oil or kerosene, coal tar oils and oils of vegetable or animal origin, also hydrocarbons, such as alkylated naphthalenes or tetrahydronaphthalene, optionally with the use of xylene mixtures, cyclohexanols, ketones, also chlorinated hydrocarbons, such as trichloroethane and tetrachloroethane, trichloroethylene or tri- and tetrachlorobenzenes. Organic solvents whose boiling points are above $100^\circ C$ are used with advantage.

Aqueous application forms are prepared most conveniently from emulsion concentrates, pastes or wettable powders by adding water. Suitable dispersants are non-ionogenic products, for example condensation products of aliphatic alcohols, amines or carboxylic acids with a long chain hydrocarbon radical containing approx. 10 to 20 carbon atoms and ethylene oxide, such as the condensation product of octadecyl alcohol and 25 to 30 mols of ethylene oxide, or that of soya fatty acid and 30 mols of ethylene oxide, or that of dodecylmercaptan and 12 mols of ethylene oxide. Among the anionic dispersants which can be used there may be mentioned, for example: the sodium salt of dodecyl alcohol sulphuric acid ester, the sodium salt of dodecylbenzenesulphonic acid, the potassium or triethanolamine salt of oleic acid or abietic acid or of mixtures of these acids, or the sodium salt of a petroleum sulphonic acid. Suitable cationic dispersants are quaternary ammonium compounds such, for example, as cetylpyridinium bromide or dioxyethylbenzyl-dodecyl ammonium chloride.

Talcum, kaolin, bentonite, calcium carbonate, calcium phosphate, also charcoal, cork powder, saw dust, and other materials of vegetable origin may be used as solid carriers to manufacture dusts and tracking powders. The manufacture of preparations in granule form is also very useful. In the conventional way, it is possible to add to the various application forms substances which improve the

distribution, adhesion, stability towards rain or the penetration capacity. Exemplary of such substances are: fatty acids, resins, glue, casein or alginates.

5 The salts of the compounds of the formula I with inorganic acids are formulated with particular advantage as soluble powders (SP). These soluble powders consists, for example, of a salt of the active substance, for example, 10 the hydrochloride, a sodium or potassium salt of an inorganic acid such, for example, as sodium chloride, and optionally a solid carrier and/or wetting agent.

15 The content of active substance in the above described agents is between 0.05 to 95%, in which connection it should be mentioned that on application from an aircraft or by means of other suitable application devices, concentrations of up to 99.5% or even pure active substance can be used.

20 The rates of application of the compounds of the formula I vary within wide limits, for example between 0.1 to 15 kg per hectare; but preferably 0.5 to 10 kg of active substance per 25 hectare are used.

Example 1.

a) N - 2 - methyl - 4 - chlorophenyl - imino-
formic acid ethyl ester
1.2 Kg. of 5 - chloro - 2 - amino - toluene
30 and 2000 ml of o-formic acid triethyl ester were heated to 140° C and the resulting alco-

hol was distilled off. Upon completion of the distillation, the residue was allowed to cool to below 80° C, 0.5 ml of concentrated sulphuric acid was added and the temperature maintained at 140° C until no further alcohol distilled over.

The crude product was purified by distillation in vacuo: b.p. 129—132° C at 15 mm Hg; yield: 1.406 kg.

b) N - (2 - methyl - 4 - chlorophenyl) - N'-methylformamidine

A 100% excess of methylamine gas was introduced within 2 hours into a solution of 58.2 g of N - 2 - methyl - 4 - chlorophenyl-imino - formic acid ethyl ester in 100 ml of anhydrous toluene. The mixture was subsequently refluxed for 3 hours. The resulting precipitate was recrystallised from hexane: b.p. 94—95° C; yield: 38.5 g (compound No. 1).

c) N - (2 - methyl - 4 - chlorophenyl) - N'-methylformamidine hydrochloride

60 g of N - (2 - methyl - 4 - chlorophenyl)-N' - methylformamidine were dissolved in 500 ml of absolute ether and treated dropwise with 42.6 ml of a 7.75N hydrochloric acid solution in dioxane. The precipitated crystals were collected by suction filtration and dried. M.p. 201—203° C; yield: 61 g (compound No. 2).

The following compounds were manufactured analogously:

- | | |
|---|----------------|
| 3) N-(2-methyl-4-chlorophenyl)-N'-ethylformamidine | m.p. 86°C |
| 4) N-(2-methyl-4-chlorophenyl)-N'-n-propylformamidine | m.p. 80°C |
| 5) N-(2-methyl-4-bromophenyl)-N'-methylformamidine | m.p. 105—107°C |
| 6) N-(2-methyl-4-bromophenyl)-N'-methylformamidine-hydrochloride | m.p. 219—222°C |
| 7) N-(2-methyl-4-bromophenyl)-N'-ethylformamidine | m.p. 93—95°C |
| 8) N-(2-methyl-4-bromophenyl)-N'-ethylformamidine-hydrochloride | m.p. 186—187°C |
| 9) N-(2-methyl-4-bromophenyl)-N'-n-propylformamidine | m.p. 85—87°C |
| 10) N-(2-methyl-4-bromophenyl)-N'-n-propylformamidine-hydrochloride | m.p. 149—150°C |
| 11) N-(2-methyl-4-iodophenyl)-N'-methylformamidine | m.p. 119—120°C |
| 12) N-(2-methyl-4-iodophenyl)-N'-methylformamidine-hydrochloride | m.p. 242—243°C |

13) N-(2-methyl-4-iodophenyl)-N'-ethylformamidine	m.p. 104—106°C
14) N-(2-methyl-4-iodophenyl)-N'-ethylformamidine-hydrochloride	m.p. 172—174°C
15) N-(2-methyl-4-iodophenyl)-N'-n-propylformamidine	m.p. 94—96°C
16) N-(2-methyl-4-iodophenyl)-N'-n-propylformamidine-hydrochloride	m.p. 156—158°C
17) N-(2-methyl-4-fluorophenyl)-N'-methylformamidine-hydrochloride	m.p. 126—127°C

Example 2.

Dust

5 Equal parts of an active substance of the formula I and precipitated silica are finely ground. By mixing the ground product with kaolin or talcum dusts having a preferred active substance content of 1—6% are manufactured.

10 Wettable powder

The following components, for example, are mixed and finely ground in order to manufacture a wettable powder:

- 15 50 parts of the active substance of the formula I
- 20 parts of highly adsorptive silica
- 25 parts of bolus alba (kaolin)
- 1.5 parts of sodium 1 - benzyl - 2 - stearylbenzimidazole - 6,3' - disulphonate
- 20 3.5 parts of the reaction product of p-tert. octylphenol and ethylene oxide

Emulsion concentrate

25 Easily soluble active substances are formulated as emulsion concentrate according to the following prescription:

- 20 parts of the active substance of the formula I
- 70 parts of xylene
- 30 10 parts of a mixture of a reaction product of an alkyl phenol with ethylene oxide and calcium dodecylbenzene sulphonate

are mixture. A sprayable emulsion is obtained by diluting the mixture with water to the desired concentration.

35 Granules

a) 7.5 g of one of the active substances of the formula I are dissolved in acetone and the resulting acetonic solution is poured on to 92 g of granulated attapulgit. The whole is mixed and the solvent is stripped off in a rotary evaporator. Granules having 7.5% content of active substance are obtained.

b) In order to manufacture 10% polymer granules, 1050 to 1100 g of industrial active substance of the formula I are dissolved in 2 litres of trichloroethane and in a fluidised bed granulator sprayed at 1.5 gauge pressure onto 9230 g of ready prepared porous urea/HCHO granules. The solvent can be removed again by heating the air spirals to approx. 50° C.

c) In order to manufacture 7.5% charged granules, 770 g of a solid industrial active substance of the formula I, 500 g of BaSO₄, 1000 g of urea and 7730 g of powdered, porous polyacrylonitrile are moulded on a roller mill and subsequently crushed to the desired particle size.

Soluble powder (SP)

In order to manufacture a soluble powder, the following components are mixed and finely ground:

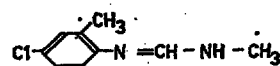
- 60 parts of a salt of an active substance of the formula I
- 36 parts of sodium chloride
- 4 parts of highly adsorptive silica.

Example 3.

Activity against *Chilo suppressalis*

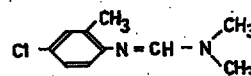
Test substances

A)



Compound No. 1

B)



Belgian Patent 642,655

The compounds were processed to granules in accordance with Example 2.

Experimental procedure

Six rice plants each of the variety Caloro were transplanted in plastic pots, which had a diameter of 17 cms at the top, and raised to a height of approx. 60 cms. Infestation with L_1 larvae (3—4 mm long) took place 2 days after the granules had been applied to the paddy water (rate of application: 8 kg of

active substance per hectare), the larvae being applied behind the second leaf of the plant. Evaluation of the insecticidal activity took place in each case 10 days after application of the granules.

Infestation 2 days after application of the granules; 5 L_1 stages per plant, 3 plants per paddy, 2 repeats (a, b).

TABLE

8 kg/ha	Repeat	Plant	Living	Escaped	Dead larvae
A	a	1	1	0+3*	1
		2	0	1	4
		3	1(↓)	1	3
	b	1	0	0+1*	4
		2	0	1	4
		3	0	4	1
B	a	1	0	1+4*	0
		2	2(↓)	2*	1
		3	2(↓)	2+1	0
	b	1	0	1	4
		2	0	2	3
		3	1(↓)	1+1*	2
Control c			11	4	0

(↓)=larvae attacked;

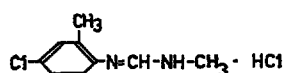
*=larvae lost through some other action than that of the test preparation.

Example 4.

Activity against *Chilo suppressalis*

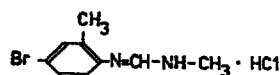
20 Test substances

A)



Compound No. 2

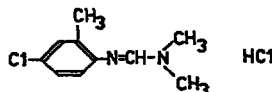
B)



Compound No. 6

C)

25



Hydrochloride of the compound B of Example 3

Experimental procedure

Rice plants of the variety Caloro were raised to a height of approx. 60 cms.

The active substance was applied by pipetting 0.1% aqueous active substance solutions (relative to the free base) into the paddy water; the rate of application corresponded to 8, 4 and 2 kg of active substance per hectare.

Infestation with L_1 larvae (3—5 mm long) took place 24 hours after the treatment, the larvae being applied behind the 2nd leaf of the plant. Evaluation of the insecticidal activity took place in each case 10 days after the treatment.

Three tests with 5 larvae on each occasion and rates of application of 8, 4 and 2 kg/ha were carried out for each active substance.

The average percentage kill of the larvae was ascertained and the results summarised in the following table:

Results

Compound	Average percentage kill of larvae
A	33.3
B	46.6
C	13.3

WHAT WE CLAIM IS:—

1. A method of combating paddy stem borers which comprises treating said paddy stem borers or their locus or habitat with a compound of the formula I

Experimental procedure

Six rice plants each of the variety Caloro were transplanted in plastic pots, which had a diameter of 17 cms at the top, and raised to a height of approx. 60 cms. Infestation with L_1 larvae (3—4 mm long) took place 2 days after the granules had been applied to the paddy water (rate of application: 8 kg of

active substance per hectare), the larvae being applied behind the second leaf of the plant. Evaluation of the insecticidal activity took place in each case 10 days after application of the granules.

Infestation 2 days after application of the granules, 5 L_1 stages per plant, 3 plants per paddy, 2 repeats (a, b).

TABLE

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	b	1	0	0+1*	4
		2	0	1	4
		3	0	4	1
B	a	1	0	1+4*	0
		2	2(↓)	2*	1
		3	2(↓)	2+1	0
	b	1	0	1	4
		2	0	2	3
		3	1(↓)	1+1*	2
Control			11	4	0

(↓)=larvae attacked;

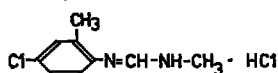
*=larvae lost through some other action than that of the test preparation.

Example 4.

Activity against *Chilo suppressalis*

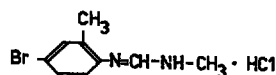
Test substances

A)



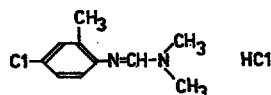
Compound No. 2

B)



Compound No. 6

C)



Hydrochloride of the compound B of Example 3

Experimental procedure

Rice plants of the variety Caloro were raised to a height of approx. 60 cms.

The active substance was applied by pipetting 0.1% aqueous active substance solutions (relative to the free base) into the paddy water; the rate of application corresponded to 8, 4 and 2 kg of active substance per hectare.

Infestation with L_1 larvae (3—5 mm long) took place 24 hours after the treatment, the larvae being applied behind the 2nd leaf of the plant. Evaluation of the insecticidal activity took place in each case 10 days after the treatment.

Three tests with 5 larvae on each occasion and rates of application of 8, 4 and 2 kg/ha were carried out for each active substance.

The average percentage kill of the larvae was ascertained and the results summarised in the following table:

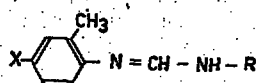
Results

Compound	Average percentage kill of larvae
A	33.3
B	46.6
C	13.3

WHAT WE CLAIM IS:—

1. A method of combating paddy stem borers which comprises treating said paddy stem borers or their locus or habitat with a compound of the formula I





(I)

wherein

- R represents an alkyl group containing maximally 4 carbon atoms, and
- 5 X represents a fluorine, chlorine, bromine or iodine atom, or with a salt of such a compound with an inorganic acid.
- 10 2. A method of combating the deleterious attack or infestation of rice cultures or paddy-fields by paddy stem borers so as to improve the economic yield thereof which comprises treating said rice cultures or paddy-fields with a compound of the formula I as defined in
- 15 claim 1 or with a salt of such a compound with an inorganic acid.
3. A method as claimed in claim 1 or claim 2 wherein the paddy stem borers are of the species *Chilo suppressalis*, *Chilo diffusilinea*,
- 20 *Chilo portellus*, *Chilothera auricilia*, *Chilothera polychrysa*, *Tryporyza incertulas*, *Tryporyza innotata*, *Sesamia inferens*, *Sesamia cretica* or *Sesamia calamistis*.
- 25 4. A method as claimed in any one of claims 1 to 3 wherein, in the compound of the formula I, R represents an alkyl group containing maximally 3 carbon atoms.

5. A method as claimed in claim 4 wherein R represent a methyl group.

6. A method as claimed in any one of claims 1 to 5 wherein, in the compound of the formula I, X represents a fluorine, bromine or iodine atom.

7. A method as claimed in claim 6 wherein X represents a bromine atom.

8. A method as claimed in any one of claims 1 to 5 wherein, in the compound of the formula I, X represents a chlorine atom.

9. A method as claimed in any one of claims 1 to 3 wherein the compound N - (2 - methyl - 4 - chlorophenyl) - N' - methylformamidine or its hydrochloride salt is employed.

10. A method as claimed in any one of claims 1 to 3 wherein the compound N - (2 - methyl - 4 - bromophenyl) - N' - methylformamidine or its hydrochloride salt is employed.

11. A method as claimed in any one of claims 1 to 3 wherein any one of the compounds numbers 3, 4 and 7 to 10 hereinbefore specifically described in Example 1 is employed.

12. A method as claimed in any one of claims 1 to 3 wherein any one of the compounds numbers 11 through 17 hereinbefore specifically described in Example 1 is employed.

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