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(54) **Insecticidal compositions**

(57) Insecticidal compositions comprising agriculturally acceptable salts of cartap, thiocyclam or nereistoxine and an agriculturally acceptable water soluble base such as calcium oxide or sodium carbonate for use against insects, particularly against Psylla spp., Myzus, Phorodon humuli and Heliothis spp., and methods for combatting such insects, especially with aqueous sprays comprising such compositions.

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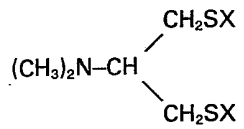
SPECIFICATION

Improvements in or relating to organic compounds

The present invention relates to novel compositions and the use of such compositions in combatting insects.

More specifically, the present invention provides an insecticidal composition comprising a component a) which is a compound of formula I



I

wherein either both X's are identical and are $CONH_2$ or both X's together form a bivalent S or a single bond in agriculturally acceptable salt form and component b) which is an agriculturally acceptable water soluble base capable of converting component a) into its free base form in aqueous medium.

The compound of formula I, wherein both X's are identical and are $CONH_2$, is an insecticide known under the common name cartap.

The compound of formula I wherein both X's together form a bivalent S is an insecticide known under the common name thiocyclam.

The compound of formula I wherein both X's together form a single bond is an insecticide known under the name nereistoxine.

For various reasons, i.a. stability, ease of formulation etc., cartap, thiocyclam and nereistoxine are formulated in agriculturally acceptable salt form, e.g. as hydrogen oxalate or as hydrochloride. Thiocyclam and nereistoxine are usually used as hydrogenoxalate, cartap as monohydrochloride.

It has now been found that the compounds of formula I are significantly more effective when applied in free base form and the compositions of the present invention represent an excellent practical means to enable the application of said free base form.

Bases suitable for use in the composition of the invention are agriculturally acceptable organic or inorganic bases. Their solubility in water is preferably at least 1g/1 and their pKa value lies preferably between 7 and 13, more preferably between 8 and 12.

Especially suitable inorganic bases are NH_4OH, $NaHCO_3$, NaOH, $Ca(OH)_2$, CaO, Na_2CO_3 or mixtures thereof and particularly CaO and Na_2CO_3. When Na_2CO_3 is used as component b) it is preferably anhydrous.

Suitable organic bases are especially organic amines of low volatility, particularly secondary or tertiary amines. The organic bases have preferably a boiling point of more than 120°C at normal atmospheric pressure (760 mm of Hg), preferably of more than 150°C. Examples of appropriate organic bases are morpholine, diethylaminoethanol, especially mono-, di- or triethanol-amine, particularly the latter.

The compositions of the invention are intended for application in aqueous spray form.

The amount of component b) to be used will depend on the water quality available where the spray broth is prepared.

In general satisfactory results are obtained when the compositions of the invention comprise component b) in an amount sufficient to be able to convert at least 80% preferably at least 90% and particularly 100% of component a) to its corresponding base form.

The type and the amount of component b) to be used will preferably be chosen so that the spray broth attains, most preferably within a short time, e.g. within 10 minutes, preferably within 5 minutes, a pH of at least 7.0, preferably of at least 7.5, particularly of about 8, e.g. of 7.7 to 9.0, the pH preferably not exceeding a pH of 10.

In view of the above and for pratical reasons, the amount of component b) to be used in the composition of the invention may also be expressed in % by weight, and varies preferably between 20 and 120%, e.g. 40% by weight of component a). When component b) is formulated in admixture with component a), the amount of component b) should for compounding technical reasons, preferably vary between 3% by weight and 20% by weight, more preferably between 4% and 20% by weight of the composition of the invention, thereby bearing in mind that the spray broth to be applied should preferably attain a pH of at least 7.5.

The compositions of the present invention may be produced in a manner known *per se* by bringing component b) in physical relationship with component a), e.g. by mixing component a) with component b) and optionally other formulating ingredients e.g. carriers, diluents and/or surfactants, or by providing a twin-pack, one section thereof comprising component a) the other comprising component b), optional formulating ingredients then preferably being in the section containing component a).

The insecticidal compositions of the invention can be in liquid or in solid form, preferably the latter especially when component b) is solid. They contain preferably 8% by weight or more, e.g. 10 to 65% by weight of component a). Preferred solid forms of the compositions of the invention are soluble and wettable powders, especially those containing 10 to 40% by weight, particularly those containing 10 to 30% by weight of component a). Other preferred compositions of the invention are those comprising more than 30% by weight of component a), particularly those comprising 40% by weight or more of component a) in twin-pack form.

When component b) is in liquid form, it may be absorbed on a suitable carrier, e.g. silica, most preferably in a weight proportion liquid component b): carrier of approximately 1:1, e.g. from 1:0.67 to 1:1.2, and be mixed with component a), or held separate thereof in the form of a twin-pack.

The compositions of the present invention preferably comprise agriculturally acceptable anionic and/or non-ionic surfactants, said surfactants acting as wetting, dispersing and emulsifying agents, assisting i.a. dispersion of component a) in the spray and improving wetting of waxy foliage and the like by the spray. Thus they aid in convenience, accuracy and effectiveness in use. When said compositions are in the form of a twin-pack, they preferably contain

the surfactant agent(s) in admixture with component a).

The anionic and/or non-ionic surfactants suitable for use in the compositions of the invention are especially agriculturally acceptable dispersing agents or emulsifiers or mixtures thereof.

Examples of suitable anionic and/or non-ionic emulsifiers are phosphoric acid esters of ethoxylated fatty alcohols, alkylarylsulphonates such as calcium dodecylphenylsulphonate, mixtures of mono- and di-esters of orthophosphoric acid, ethoxylated sorbitan fatty esters polyglycol ethers e.g. alkylphenyl polyethylene glycol ethers such as nonylphenol-polyglycol ether, polyoxyethylene triglycerides, polyoxyethylene / polyoxypropylene copolymers or mixtures thereof.

Preferred emulsifiers have an average HLB (hydrophilic-lipophilic balance) of from 9 to 15.

Examples of suitable dispersing agents are fatty alcohol sulphates such as Na lauryl sulphate, lignin sulphonates, naphthalene sulphonate / formaldehyde condensates, Na N - methyl - N - oleoyl taurate.

Examples of commercially available anionic and/or non-ionic surfactants especially suitable for use in the compositions of the invention are ATLOX 1285 (a non-ionic polyoxyethylene triglyceride having an HLB-value of 14.4, an acid number of max. 1.5-1.8, a saponification number of 40-50 and an hydroxyl number of 50-65; Atlas Chemie GmbH), ANTAROX CO-880 (a non-ionic polyoxyethylenated nonylphenol comprising 30 mols of ethylene oxide per mol of nonylphenol, General Aniline and Film Co.), PLURONIC F 108 (a non-ionic polyoxyethylene / polyoxypropylene block polymer having a basic polyoxypropylene moiety with a molecular weight of approximately 3.250, the total molecule comprising about 80% by weight polyoxyethylene groups; BASF, Wyandotte Co.), more preferably GAFAC RS 710 (an anionic mixture of mono- and diesters of orthophosphoric acid with a polyethoxylated fatty alcohol having a density of 1.04-1.06 and an acid number of 60-75; General Aniline and Film Co.), RESOLIN C (a Na dodecylphenyl sulphonate; SANDOZ AG), most preferably ATLOX 4851 B (a blend of Ca alkylarylsulphonate and a polyethoxylated triglyceride, the mixture having an HLB-value of ca. 12.5, an acid number of max. 1.5 and a viscosity at 25°C of 300-700 cps; Atlas Chemie GmbH), TENSIOFIX KL (an anionic Ca alkylarylsulphonate having a density, at 20°C of about 1.042; Tensia, Belgium), FENOPON T 77 (Na N - methyl - N - oleoyl taurate; General Aniline and Film Co.) and ANTAROX CO 210 (a non-ionic polyoxyethylated nonylphenol comprising about 1½ mols of ethylene oxide per mol of nonylphenol; General Aniline and Film Co.).

The optimal amount of surfactant will, of course, vary depending on the target insect species. Favourable biological activity is in general obtained with compositions comprising a weight ratio component a): surfactant in the range of 1:0.04-6, preferably 1:0.1-1, particularly 1:0.15-0.6 e.g. 1:0.5.

The amount of surfactant in the composition is preferably chosen in such a way that the spray broth (liquor) to be applied contains from 0.01% up to 0.4% by weight of surfactant, the amount of surfactant being in inverse proportion to the volume of spray broth to be applied; a low volume spray broth containing e.g. 0.05 up to 0.4% by weight of surfactant whereas a high volume spray broth may contain e.g. from 0.01% up to 0.1% by weight surfactant.

When the surfactant is in liquid form, it may be absorbed on a suitable carrier, e.g. silica, as indicated for component b).

The compositions of the invention generally contain 20 to 99% by weight of the ingredients component a), component b) and optional surfactant, whereby those comprising component b) in admixture with component a) preferably contain 20 to 80%, more preferably 30 to 80%, by weight of said ingredients.

The improved insecticidal activity of component a), particularly of the agriculturally acceptable acid addition salts of thiocyclam, expecially of thiocyclam hydrogen oxalate when employed in conjunction with component b) and optionally an anionic or non-ionic surfactant, according to the invention is indicated by the usual standard tests such as the Spray - Potter - Tower test on Colorado potato beetle larvae and by treatment of Leptinotarsa, Heliothis or Spodoptera eggs and also by field trials such as treatment of rice cultures, cotton, hops, peaches, pears, potatoes and sugar beet.

Very satisfactory results are obtain against insects of the order Thysanoptera, e.g. those of the family Thripidae; of the order Heteroptera, e.g. those of the family Pentatomidae; of the order Orthoptera, e.g. those of the family Gryllidae, and especially against insects of the order Homoptera, particularly sucking pests of the families Delphacidae, Cicadellidae, Aphididae, Psyllidae and Coccidae; of the order Lepidoptera, particularly those of the families Geometridae, Yponomeutidae, Gelechiidae, Pyralidae, Pieridae, Plutellidae, Noctuidae (e.g. Heliothis, Spodoptera, Alabama), Tortricidae, Cossidae, Heliozelidae, Hepialidae, Hesperiidae, Lymantriidae, Lyonetiidae, Nepticulidae, Oecophoridae; of the order Coleoptera, particularly those of the families Chrysomelidae, Curculionidae, Coccinellidae, Nitidulidae, Elateridae; of the order Diptera, particularly those of the families Agromyridae, Itonididae and Chironomidae; and of the order Hymenoptera, particularly those of the families Tenthredinidae, Cephidae and Cimbicidae.

In view of their insecticidal activity, the compositions of the invention are especially indicated for use in combatting (including preventing) insects in a locus, especially against the insects indicated hereinbefore, particularly in a plant locus, especially in cereals such as rice and corn (maize), in fibre crops such as cotton, in sugar crops such as sugar cane and sugar beet, in oil crops such as rape, in fruit crops such as pip fruits (e.g. pears), stone fruits (e.g. peaches) and citrus fruits (e.g. lemons), in vegetables such as potatoes, cruciferous vegetables (e.g. broccoli, brussels sprouts) and solonaceous vegetables (e.g. paprika, tomatoes), in beverages or spice crops such as tobacco, hop, tea, coffee and cocoa.

The invention consequently provides also a method of combatting insects in a locus, particularly in a plant locus, preferably in a plant locus as indi-

cated hereinbefore, which comprises applying to the locus, separately or in admixture, in an insecticidally effective amount, component a) and component b).

The amount of component a) to be employed depends on various factors such as the nature of component a), the species to be combatted, the locus, e.g. development stage of the insect and leaf mass of the plant locus, the time and type of application. In general, the desired effect is obtained when component a) is used in the method of the invention at a dosage rate of from 150 g to 1000 g per hectare of plant locus, whereby usually, especially when agriculturally acceptable acid addition salts of thiocyclam are used as component a), the dosage rate need not exceed 400 g/ha, unless under extreme conditions e.g. when severe infestation exists or when insects that are difficult to combat, such as Tortricidae are present.

Pests against which the method of the invention is indicated to be particularly of interest when agriculturally acceptable acid addition salts of thiocyclam as component a) are used, include by way of illustration *in rice:* at a dose range of 200 to 500g, preferably of 300 to 400g/ha Thysanoptera, especially of the family Thripidae, particularly Thrips oryzae Will.: Heteroptera, especially of the families Pentatomidae and Coreidae, particularly Scotinophara lurida Burm. and Leptocorisa acuta Thunb.; Homoptera of the families Delphacidae, Cicadellidae, Aphididae, especially Nilaparvata lugens Stål, Nilaparvata oryzae Mats., Sogata distincta Dist., Calligypona furcifera Horv., Nephotettix bipunctatus F., Nephotettix apicalis Motsch, Sipha glyceriae Kalt., Rhopalosiphon oryzae Mats.; Coleoptera of the family Chrysomelidae, especially Lema oryzae Kuw.; Lepidoptera of the families Pyralidae, Noctuidae and Hesperiidae, especially Trypcryza (Schoenobius) incertulas Walk., Chilo suppressalis Walk., Chilo plejadellus Zck., Chilo zonellus Swinh., Chilotraea auricilia Dudg., Chilotraea (Proceras) polychrysa Meyr., Scirpophaga innotata Walk., Cnaphalocrocis medinalis Guen., Sesamia inferens Walk., Parnara guttata Brem., Parnara mathias F.; Diptera of the families Itonididae, Chloropidae, Agromyzidae and Ephydridae, especially Pachydiplosis oryzae W.-M., Chlorops oryzae Mats., Agromyza oryzae Mun. and Hydrellia griseola Fall.,

in cotton: at a dose range of 200 to 400g/ha, Homoptera, especially those of the family Aleyrodidae, particularly Bemisia tabaci Genn.; Coleoptera, especially of the family Chrysomelidae, particularly Podagrica pallida Jac., Podagrica puncticollis Weise, Syagrus rugrifrons Baly., Syagrus calcaratus F. and Syagrus morio Harr.; Lepidoptera, especially those of the families Lyonetiidae, Gracilariidae, Gelechiidae, Tortricidae, Pyralidae and Noctuidae, particularly Bucculatrix thurberiella Busck, Acrocercops bifasciata Wals., Platyedra gossypiella Saund., Argyroploce leucotreta Meyr., Syllepta derogata F., Mescinia peruella Schaus, Phycita infusella Meyr., Alabama argillacea Hbn., Heliothis spp (especially eggs and small larvae), Earias spp. (especially eggs and small larvae), Spodoptera spp (especially eggs and small larvae) and Laphygma spp.,

in hops: with a spray broth comprising 20 to 40 g component a) per hectolitre, Homoptera, especially those of the family Aphididae, particularly Phorodon humuli,

in stone fruits: with a spray broth comprising 20 to 100 g component a) per hectolitre, Homoptera, especially those of the families Cicadellidae and Aphididae, particularly Typhlocyba spp., Erythroneura spp., Hyalopterus pruni Koch, Hysteroneura setariae Ths., Brachycaudus persicaecola Bdv., Myzus cerasi F. and Myzus persicae Sulz; Coleoptera, especially of the family Chrysamelidae, particularly Nodonota puncticollis Say, Galerucella cavicollis LeC.; Lepidoptera, especially of the families Lyonetiidae, Hyponomeutidae, Gelechiidae, Tortricidae, Cossidae, Pyralidae, Geometridae, Arctiidae, Lyamtriidae and pieridae, particularly Lyonetia clerkella L.; Hymenoptera, especially of the families Tenthredinidae and Pamphiliidae, particularly Caliroa spp., Hoplocampa spp. and Neurotoma nemoralis L.;

in pip fruits: with a spray broth comprising 20 to 100 g component a) per hectolitre, Homoptera, especially those of the families Cicadellidae, Psyllidae and Aphididae, particularly Empoasca maligna Walsh, Psylla spp., (e.g. Psylla piri L., Psylla piricola Först., Psylla pirisuga Först), Sappaphis piri Mats.,

in rape: with a dose range of 100 to 300 g component a) per ha, Coleoptera, especially of the families Nitidulidae and Curculionidae particularly Meligethes aeneus F. and Ceuthorrhynchus spp.; Hymeoptera, especially of the family Tenthredinidae, particularly Athalia rosae L.

in potato: with a dose range of 100 to 300 g component a) per ha, Thysanoptera, especially of the family Thripidae, particularly Hercothrips sundanensis B. and C., Thrips tabaci; Homoptera especially of the families Cicadellidae, Aleyrodidae and Aphididae, particularly Empoasca fabae Harr., Circulifer tenellus Baker, Bemisia tabaci Genn., Trialeurodes vaporariorum Westw., Aphis nasturtii Kalt., Macrosiphum spp. and Myzus persicae Sulz; Coleoptera, especially of the family Chrysomelidae, particularly Diabrotica spp., Epithrix cucumeris Harr., Leptinotarsa decemlineata Say, Phyllotreta pusilla Horn.; Lepidoptera, especially of the families Gelechiidae and Pyralidae, particularly against Phthorimaea operculella Zell. and Ostrinia nubilalis Hbr.; Diptera, especially of the family Agromyzidae, particularly Liriomyza spp.,

in corn (maize): with a dose range of 200 to 600 g component a) per ha, Homoptera, especially those of the families Fulgoridae and Aphididae, particularly Pyrilla spp. and Rhopalosiphon maidis Fitch; Coleoptera, especially those of the family Chrysomelidae, particularly Chaetocnema pulicaria Melsh., Lema melanopus L., Diabrotica balteata LeC. and Diabrotica decolor Er.; Lepidoptera, especially those of the families Pyralidae and Hesperiidae, particularly Ostrinia (Pyrausta) nubilalis Hbn., Chilo. suppressalis Walk., Cnaphalocrocis medinalis Guen., Diatraea crambidoides Grote, Diatraea saccharalis F. and Parnara guttata Brem.,

in sugar beet: with a dose range of 200 to 600 g component a) per ha, Homoptera, especially those of the families Cicadellidae and Aphididae, particularly

Aceratagallia sanguinolenta Prov., Circulifer tenellus Baker, Aphis fabae Scop., macrosiphum euphorbiae Ths. and Myzus persicae Sulz.; Coleoptera, especially those of the families Silphidae, Chrysomelidae, Curculionidae and Cryptophagidae, particularly Blitophaga spp. (such as Blitophaga opaca L. and Blitophaga undata Müll), Chaetocnema tibialis Ill., Lixus spp. (such as Lixus junci Boh. and Lixus ascanii L.) and Bothynoderes punctiventris Germ.; Lepidoptera, especially those of the families Gelechiidae and Pyralidae, particularly Phthorimaea ocellatella Boyd, Loxostege sticticalis L., Psara bipunctalis F.; Diptera, especially those of the family Anthomyiidae, particularly Pegomyia hysocyami betae Curt.; Hymenoptera, especially those of the family Tenthredinidae, particularly Athalia rosae L.

The composition of the invention are preferably applied as a tank mix. The invention also provides aqueous application forms comprising the compositions of the invention.

In general the aqueous application forms may contain between 0.01% and 0.8% (10 to 800 g/hl) by weight of component a) depending on the application method (spray volume). For use in field crops such as corn, cereals, cotton, rape, potato, sugar beet, rice the spray broth comprises preferably 0.01% to 0.6%, particularly 0.015 to 0.2% by weight of component a). Good results are in general also obtained in vegetables with concentrations of 0.01% to 0.06%, in citrus fruits and coffee 0.02 to 0.1% and in tea 0.02 to 0.04% by weight of component a).

The method of the invention is particularly effective against sucking pests especially of the order Homoptera, particularly against Myzus persicae, Pysila spp, Phorodon humuli, Aleutroxis floccosus, Nilaparvata spp, especially Nilaparvata lugens and against heliothis spp.

Specific examples of formulations according to the invention are given below. Parts are by weight.

Formulation A — Soluble Powder

10 Parts of an emulsifier e.g. ANTAROX CO-210 are added to 7 parts of a carrier e.g. silica in a mixer and mixed for 30 minutes. 74 Parts of technical thiocyclam hydrogenoxalate (comprising ca. 88% thiocyclam hydrogenoxalate) and 9 parts of a base, e.g. CaO are added thereto, the mixture mixed for 20 minutes and then milled in a hammer mill.

Formulation B — Wettable Powder

28 Parts thiocyclam hydrogenoxalate (technical), 12 parts of a surfactant (e.g. FENOPON T-77), 8 parts of a carrier, e.g. silica, 15 parts clay, 4 parts of base, e.g. CaO and 33 parts Na_2SO_4 are mixed together for one hour. The mixture is milled in a hammer mill to get a wettable powder.

Formulations C, D, E and F

One proceeds as described in the Formulation Examples A and B, replaces, however, the thiocyclam hydrogenoxalate by the same amount (parts) of cartap (in monohydrochloride form) or nereistoxine hydrogenoxalate to obtain Formulation C (soluble powder cartap); Formulation D (wettable powder cartap); Formulation E (soluble powder; nereistoxine hydrogenoxalate) and Formulation F (wettable powder; nereistoxine hydrogenoxalate).

Formulations G to K — Soluble Powder

Analogous to formulation Example A are obtained the following formulations.

	% by weight				
Formulation	*G*	*H*	*I*	*J*	*K*
Thiocyclam hydrogenoxalate (techn.)	68.5	28.4	28.4	46.5	68.5
ATLOX 4851 B	7.25	10.8	10.8	18.0	7.25
Silica	7.25	7.2	7.2	12.0	7.25
CaO	10.00	4.0	20.0	9.0	10.0
Fumaric acid	4.00	–		–	–
Ethylene diamine tetra acetic acid	3.00	–		–	–
NaCl	–	49.6	33.6	14.5	7.0

Formulation L

16 Parts of an emulsifier, e.g. ATLOX4851 B, and 16 parts of monoethanolamine are blended in a mixer with 23 parts of silica. A free flowing powder is obtained. 45 Parts of thiocyclam hydrogenoxalate (Technical) are added thereto and the mixture is milled in a hammer mill.

Formulation M — Tank mix

30 g of morpholine are added to 100 litres of water. To this solution are added, while stirring, 100 g of a composition comprising 58% thiocyclam hydrogenoxalate (technical), 20.1% ATLOX 4851 B, 13.4% silica and 8.5% NaCl. The stirring is continued until the powder is completely dissolved.

(% are by weight)

Formulation N — Tank mix

One proceeds as indicated in Formulation Example M, employing 50 g calcined Na_2CO_3 instead of 30 g morpholine.

Formulation O — Tank mix

The spray tank is filled with 100 litres of water, 40 g granulated calcined sodium carbonate (water free) are then slowly added while agitating or circulating the water until the sodium carbonate is completely dissolved. Then 80 g of the composition comprising 58% thiocyclam hydrogen oxalate (technical), 20.1% ATLOX 4851 B, 13.4% silica and 8.5% NaCl are added, while stirring, until the product is completely

dissolved.

ATLOX 4851 B used in Formulation Examples G to O is a surfactant supplied by ICI-Atlas Chemie GmbH, Germany. It is a mixture of the calcium salt of an alkylarylsulphonate with polyoxyethylenated triglyceride in the form of a yellow-brown viscous liquid having a water content of less than 1%, a density at 20°C of 1.02-1.04 g/cm³, a HLB of 13.2 ± 1.0. ATLOX 4851 B can be replaced by equivalent emulsifiers.

Example APP-1

Cotton infested with eggs of *Heliothis zea* is treated in Georgia/USA with an aqueous solution of composition G (see Formulation G example) at a rate of 136 g thiocyclam hydrogenoxalate (techn.)/ha, with a spray volume of 8 gals/acre. The effectiveness of the treatment (in %) is evaluated by determination of the dead eggs (7 days after application) according to the Abbott calculation method. The results are compared with the results obtained with a standard formulation (S) containing

95% thiocyclam hydrogenoxalate (techn.)
1% TENSIOFIX XN 10 (an ethoxylated phosphate surfactant; Tensia, Belgium)
1% silica
3% ethylene diamine tetra acetic acid

and applied at the same rate (136 g active ingredient/ha).

The following results are obtained

% effectiveness					
Test 1		*Test 2*		*Test 3*	
Formulation		Formulation		Formulation	
G	S	G	S	G	S
86	47	82	27	79	22

G = Formulation G
S = Standard

Example APP-2

Analogous improved effectiveness is found when Formulation G is replaced by a equivalent amount of Formulation A, B, C, D, E, F, H, I, J, K, L, M, N or O.

Example APP-3

The effectiveness of Formulation A in rice is compared with that of the Standard Formulation S (field tests in South Korea). The dose rate can be reduced from 600-750g active ingredient/ha with Standard (see Example APP-1; Formulation S) to 330-375 g active ingredient/ha when Formulation A is used. Formulation A is particularly effective against Pyralidae, Cicadellidae, Delphacidae and Chrysomelidae.

Example APP-4

Analogous improvement of effectivness in rice is observed when Formulation A in Example APP-3 is replaced by one of the formulations B to O.

Example APP-5

The effectiveness of Formulations A, B and G to O is compared with that of Formulation S against *Lepitinotarsa* (adults and larvae) in potato at an application range of 300 g component a) per ha. significant improvement of the effectiveness with the Formulations A, B, and G to O vis à vis Formulation S is observed.

Example APP-6

The effectiveness of Formulations A, B and G to O is compared with that of Formulation S against Phorodon humuli in hops. The formulations are applied in the form of an aqueous spray comprising 0.02% by weight of thiocyclam hydrogenoxalate (Formulations M, N and O should be diluted accordingly) until the run-off. A significant improvement of the effectiveness vis à vis Formulation S is observed.

Example APP-7

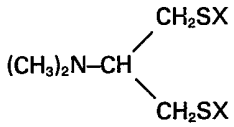
Pear trees infested with Psylla pirisuga are treated (until the run-off) with an aqueous spray comprising 0.06% by weight of thiocyclam hydrogenoxalate formulated according to Formulation Example A, B and G to L. A significant improvement of the effectiveness vis à vis Formulation S is observed.

Example APP-8

Orange trees infested with Aleurothrixus floccosus are treated (until the run-off) with an aqueous spray comprising 0.04% by weight of thiocyclam hydrogenoxalate formulated according to Formulation Examples A, B, G to L and O. A significant improvement of the effectiveness vis à vis Formulation S is observed.

CLAIMS

1. An insecticidal composition comprising a component a) which is a compound of formula I



I

wherein either both X's are identical and are $CONH_2$ or both X's together form a bivalent S or a single bond in agriculturally acceptable salt form and a component b) which is an agriculturally acceptable water-soluble base capable of converting component a) into its free base form in aqueous medium.

2. A composition according to Claim 1, wherein both X's together form a bivalent S.

3. A composition according to Claim 2, wherein component a) is in hydrogen oxalate form.

4. A composition according to any one of the claims 1 to 3, wherein component b) has a pKa value of from 7 to 13.

5. A composition according to Claim 4, wherein the pKa value is from 8 to 12.

6. A composition according to any of Claims 1 to 5 wherein component b) is an inorganic base.

7. A composition according to Claim 6 wherein component b) is NH_4OH, $NaHCO_3$, NaOH, $Ca(OH)_2$, CaO, Na_2CO_3 or mixtures thereof.

8. A composition according to Claim 7, wherein component b) is CaO.

9. A composition according to Claim 7, wherein component b) is Na_2CO_3.

10. A composition according to Claim 9, wherein the Na_2CO_3 is anhydrous.

11. A composition according to any one of

Claims 1 to 10, wherein component b) is present in an amount sufficient to be able to convert at least 80% of component a) to its corresponding base form.

12. A composition according to Claim 11, wherein component b) is present in an amount sufficient to be able to convert at least 90% of component a) to its corresponding base form.

13. A composition according to Claim 11, wherein component b) is present in an amount sufficient to be able to convert at least 100% of component a) to its corresponding base form.

14. A composition according to any one of Claims 1 to 13 for use in an aqueous spray wherein the type and amount of component b) is selected so that the spray broth attains a pH in the range of from 7.0 to 10.

15. A composition according to Claim 14, wherein the type and amount of component b) is selected so that the spray broth attains a pH of at least 7.5.

16. A composition according to Claim 15, wherein the type and amount of component b) is selected so that the spray broth attains a pH in the range of from 7.7 to 9.

17. A composition according to any one of Claims 1 to 16 comprising component b) in an amount of 20 to 120% by weight of component a).

18. A composition according to Claim 17, comprising 4 to 20% by weight of component b) in admixture with component a).

19. A composition according to any one of Claims 1 to 18 comprising an agriculturally acceptable anionic and/or non-ionic surfactant.

20. A composition according to Claim 19, wherein the surfactant is an agriculturally acceptable dispersing agent or emulsifier, or a mixture thereof.

21. A composition according to Claim 20, wherein the emulsifier is a phosphonic acid ester of ethoxylated fatty alcohols, an alkylarylsulphonate, a mixture of mono- and di-esters of orthophosphonic acid, an ethoxylated sorbitan fatty ester, an alkylphenyl polyethylene glycol ether, a polyoxyethylene triglyceride or a polyoxyethylene / polyoxypropylene copolymer.

22. A composition according to Claim 20 or 21, wherein the emulsifier has an average hydrophilic - lipophilic balance of from 9 to 15.

23. A composition according to Claim 20, wherein the dispersing agent is a fatty alcohol sulphate, a lignin sulphonate, a naphthalene sulphonate / formaldehyde condensate or is Na N - methyl - N - oleoyl taurate.

24. A composition according to any one of Claims 19 to 23, comprising a weight ratio component a): surfactant in the range of 1:0.04-6.

25. A composition according to Claim 24 wherein the weight ratio component a): surfactant is in the range of 1:0.1-1.

26. A composition according to Claim 25, wherein the weight ratio component a): surfactant is in the range of 1:0.15-0.6.

27. A composition according to any one of Claims 1 to 26 comprising 20 to 99% by weight of component a), component b) and optional surfactant.

28. A composition according to Claim 27, comprising component b) in admixture with component a) and containing 20 to 80% by weight of component a), component b) and optional surfactant.

29. A composition according to Claim 28, containing 30 to 80% by weight of component a), component b) and optional surfactant.

30. An aqueous application form of the compositions according to any one of Claims 1 to 29, wherein the concentration of component a) is between 0.01% and 0.9% by weight.

31. A method of combatting insects in a locus which comprises applying to the focus in aqueous medium, separately or in admixture, in an insecticidally effective amount, component a) as defined in Claim 1 and component b) as defined in Claim 1.

32. A method according to Claim 31, wherein component b) is an inorganic base having a pKa value of from 7 to 13.

33. A method according to Claim 32, wherein component b) is CaO.

34. A method according to Claim 32, wherein component b) is Na_2CO_3.

35. A method according to any one of Claims 31 to 34, wherein the amount of component b) applied is 20 to 120% by weight of component a).

36. A method according to Claim 35, wherein component b) is used in an amount sufficient to convert at least 80% of component a) to its corresponding base form.

37. A method according to Claim 36, wherein component b) is used in an amount sufficient to convert at least 90% of component a) to its corresponding base form.

38. A method according to Claim 37, wherein component b) is used in an amount sufficient to convert at least 100% of component a) to its corresponding base form.

39. A method according to any one of Claims 31 to 38, wherein component a) is applied in admixture with an agriculturally acceptable anionic and/or non-ionic surfactant.

40. A method according to Claim 39, wherein the surfactant is an agriculturally acceptable dispersing agent or emulsifier or a mixture thereof.

41. A method according to Claim 40, wherein the applied weight ratio component a): surfactant is in the range of 1:0.01-1.

42. A method according to any one of Claims 31 to 41, wherein the locus is a plant locus.

43. A method according to Claim 42, wherein the plant locus is a rice, sugar beet, cotton, rape seed, stone fruit, pear tree, citrus fruit, potato, cruciferous vegetable, solonaceous vegetable, hops tea, coffee or cocoa crop.

44. A method according to Claim 42 or 43, wherein the insects are Pyralidae, Noctuidae, Chrysomelidae or sucking insects of the families Delphacidae, Cicadellidae, Aphididae, Psyllidae or Aleyrodidae.

45. A method according to any of Claims 42 to 44, wherein component a) is applied at a dosage rate of from 150 to 1000 g per hectare of plant locus.

46. A method according to any of Claims 42 to 45

wherein the application form is an aqueous spray, and wherein the amount of component b) is selected so that the pH of the spray broth attains a pH in the range of from 7.0 to 10.

47. A method according to Claim 46, wherein the amount of component b) is selected so that the spray broth attains a pH of at least 7.5.

48. A method according to Claim 47, wherein the amount of component b) is selected so, that the spray broth attains a pH of from 7.7 to 9.

49. A method according to any of Claims 31 to 48, wherein component a) is a compound of formula I defined in Claim 1, wherein both X's together form a bivalent S.

50. A method according to Claim 49, wherein component a) is in hydrogen oxalate form.

51. A method according to Claim 49 or 50, wherein component a) is applied at a dosage rate of from 150 to 400 g per hectare of plant locus.

52. A method according to Claim 51, wherein the plant locus is a rice locus.

53. A method according to Claim 52, wherein the pests are Pyralidae, Cicadellidae, Delphacidae and/or Chrysomelidae.

54. A method according to Claim 51, wherein the plant locus is a cotton locus.

55. A method according to Claim 54, wherein the insect pests are Noctuidae.

56. A method according to Claim 55, wherein the pests are Alabama argillacea Hbn, Heliothis spp, Earias spp., Spodoptera spp and/or Laphygma spp.

57. A method according to Claim 51, wherein the plant locus is hops.

58. A method according to Claim 57, wherein the pest is Phorodon humuli.

59. A method according to Claim 51, wherein the pest is Myzus persicae Sulz.

60. A method according to Claim 59, wherein the plant locus is a stone fruit, sugar beet or tobacco crop.

61. A method according to Claim 51, wherein the pest is a Psylla spp.

62. A method according to Claim 61, wherein the pest is Psylla piri, Psylla piricola or Psylla pirisuga.

63. A method according to Claim 61 or 62, wherein the plant locus is a pip fruit crop.

64. A method according to Claim 63, wherein the plant locus is a pear crop.

65. A method according to any one of Claims 31 to 64, wherein component a) and component b) are applied as a tank mix.

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