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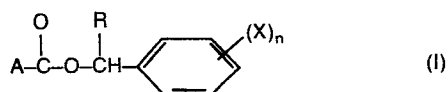
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⑤④ **Pesticidal composition and method of combating pests.**

⑤⑦ A pesticidal composition which includes:

- (a) N,N-di-(2,4-xylyliminomethyl)-methanamine, and
- (b) a pyrethroid insecticide having the general formula:



wherein A is an optionally-substituted aralkyl, alkyl or cycloalkyl group, R is hydrogen, cyano or ethynyl, X is alkyl, alkenyl, aralkyl or aryloxy and n is 1 to 5, has been shown to possess synergistic activity against mites.

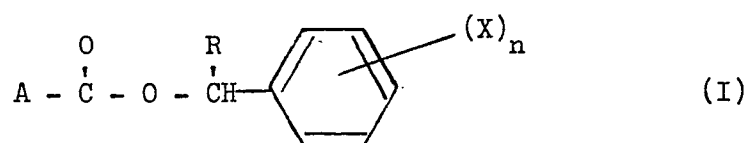
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PESTICIDAL COMPOSITION AND METHOD OF COMBATING PESTS

This invention relates to a pesticidal composition and to a method of combating pests.

The Applicant has found that a composition including the known acaricide, N,N-di-(2,4-xylyliminomethyl)-methylamine
 5 and certain pyrethroid insecticides possess synergistic activity with respect to acarid pests; that is to say, the activity of the combination of the two pesticides produces a more-than-additive pesticidal effect.

Accordingly, the present invention provides a pesticidal
 10 composition which comprises N,N-di-(2,4-xylyliminomethyl)-methylamine (hereinafter referred to as "amitraz") characterized in that the composition includes a pyrethroid insecticide having the general formula:



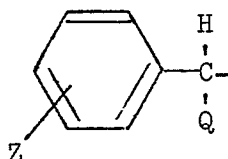
wherein A is an optionally-substituted aralkyl, alkyl or
 15 cycloalkyl group, R is hydrogen, cyano or ethynyl, X is alkyl, alkenyl, aralkyl or aryloxy, and n is 1 to 5.

Generally speaking, an alkyl, cycloalkyl or alkenyl group represented by A or X preferably contains up to 6 carbon

atoms and an aralkyl or aryloxy group represented by A or X preferably contains up to 10 carbon atoms.

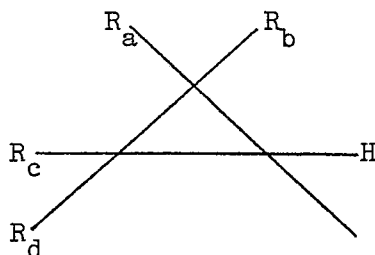
It should be noted that the pyrethroid insecticide I can exist in the form of optical isomers or cis-trans-isomers and in the composition according to the invention an individual
5 isomer or mixture of isomers including racemates may be employed.

Preferably, A represents an optionally-substituted aralkyl group in general formula I. Especially preferred compounds of the general formula I are those in which A represents a substituted benzyl group of the general formula:
10



wherein Z represents a halogen, preferably a chlorine, atom, or an alkoxy group having 1 to 4 carbon atoms, for example a methoxy group, and Q represents an alkyl group having from 1 to 6 carbon atoms, especially a branched-chain group, for example an iso-
15 propyl group. The most preferred compounds of the general formula I are those wherein A represents an alpha-isopropyl-4-chlorobenzyl group, R represents a hydrogen atom or a cyano group, n is 1, and X represents a 3-phenoxy group, for example alpha-cyano-3-phenoxybenzyl alpha-isopropyl-4-chlorophenyl
20 acetate.

If, however, A represents an optionally-substituted cycloalkyl group in general formula I, the preferred compounds of this type are those wherein A represents a cyclopropyl group of formula:



wherein R_a and R_b each individually represent an alkyl group having from 1 to 6 carbon atoms, especially methyl or a halogen, especially chlorine, bromine or fluorine atom; or R_a and R_b together represent an alkylene group having from 2 to 6, especially 3, carbon atoms; or R_a represents a hydrogen atom and R_b represents an alkenyl group having from 2 to 6 carbon atoms, especially an isobutenyl group, or a halo-alkenyl group having from 2 to 6 carbon atoms and from 1 to 3 chlorine or bromine atoms, especially a mono- or dichloro-vinyl group; R_c and R_d both represent an alkyl group having 1 to 6 carbon atoms, especially a methyl group, or R_c and R_d together represent an alkylene group having from 2 to 6, especially 3, carbon atoms. Thus, for example, A may represent a 2,2,3,3-tetramethylcyclopropyl group while R represents a hydrogen atom or a cyano group, n is 1 and X is 3-phenoxy.

The mixture of amitraz and the pyrethroid insecticide not only produces a pesticide having a markedly wider spectrum of activity than the pyrethroid or the amitraz alone, but also produces a surprising synergistic effect with respect to acarids, e.g., glasshouse red spider mite, Tetranychus urticae. The mixture also possesses useful properties with respect to the eggs of lepidopterous and acharine pests; it has uses in the agrochemical and animal health fields.

The weight ratio of the pyrethroid insecticide to amitraz may be in the range 5:1 to 1:50.

The pesticidal composition according to the invention preferably also comprises a carrier, especially at least two carriers, at least one of which is a surface-active agent.

A carrier may be a solid or liquid material, which may be inorganic or organic and of synthetic or natural origin. Typical solid carriers include natural and synthetic clays and silicates, for example, natural silicas, for example diatomaceous earths, and aluminium silicates, for example kaolinites, montmorillonites and micas. Typical liquid

carriers are ketones, for example methylcyclohexanone, aromatic hydrocarbons, for example methylnaphthalenes, petroleum fractions, for example petroleum xylenes and light mineral oils, and chlorinated hydrocarbons, for example carbon tetrachloride.

5 Mixtures of liquids are often suitable.

One or more surface-active agents and/or stickers can be included in the composition. A surface-active agent may be an emulsifying agent or a dispersing agent or a wetting agent; it may be non-ionic or ionic. Any of the surface-active agents
10 usually applied in formulating insecticides may be used. Examples of suitable surface-active agents are the sodium and calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation products of fatty acids of aliphatic amines or amides containing at least 12 carbon atoms in the molecule with
15 ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitan, sucrose or pentaerythritol, condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty alcohols or alkyl phenols, for example *p*-octylphenol or *p*-octylcresol, with ethylene oxide and/or
20 propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts
25 of sulphonated castor oil, and sodium alkylaryl sulphonates, such as sodium dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The composition of the invention may for example be
30 formulated as a wettable powder, microcapsules, a dust, granules, a solution, an emulsifiable concentrate, an emulsion, a suspension concentrate or an aerosol. The composition may have controlled release properties, or may be suitable for use as a bait.

Wettable powders usually contain 25, 50 or 75%w of active ingredient and may contain, in addition to inert solid material, 3-10%w of a dispersing agent and, where necessary, 0-10%w of a stabilizer, a penetrant and/or a sticker. A dust is usually formulated as a dust concentrate having a composition similar to that of a wettable powder but without a dispersant, and is diluted in the field with further solid carrier to give a composition usually containing $\frac{1}{2}$ -10%w of active ingredient.

Granules usually have a size in the range of from 10 to 100 BS mesh (1.676-0.152 mm) and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain $\frac{1}{2}$ -25%w active ingredient and 0-10%w of additives, for example a stabilizer, slow-release modifier and/or a binding agent.

Emulsifiable concentrates usually contain, in addition to a solvent, and, when necessary, co-solvent, 10-50%w/v active ingredient, 2-20%w/v emulsifier and 0-20%w/v of other additives, for example a stabilizer, a penetrant and/or a corrosion inhibitor. A suspension concentrate is a stable, non-sedimenting, flowable product and usually contains 10-75%w active ingredient, 0.5-15%w of dispersing agent, 0.1-10%w of suspending agent, for example protective colloid and for a thixotropic agent, and 0-10%w of other additives including, for example, a defoamer, a corrosion inhibitor, a stabilizer, a penetrant and/or a sticker, and as dispersant, water or an organic liquid in which the active ingredient is substantially insoluble; certain organic additives and/or inorganic salts may be dissolved in the dispersant to assist in preventing sedimentation or as anti-freeze for water.

The aqueous dispersions and emulsions formed by diluting a wettable powder or an emulsifiable concentrate of the invention with water, also lie within the scope of the present invention. Such dispersions and emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick "mayonaise"-like consistency.

A composition of the invention may also contain other ingredients, for example, one or more other compounds possessing pesticidal, herbicidal or fungicidal properties, or attractants, for example pheromones or food ingredients, for use in baits and trap formulations.

The invention also includes a method of combating pests at a locus characterized in that a pesticidal composition according to the invention is applied to the locus.

The invention is further illustrated by the following Example, in which the joint action of two pesticides was analyzed according to the method of Yun-Pei Sun and E.R. Johnson, Journal of Economic Entomology, 1960, Volume 53, No. 5, pp. 887-892.

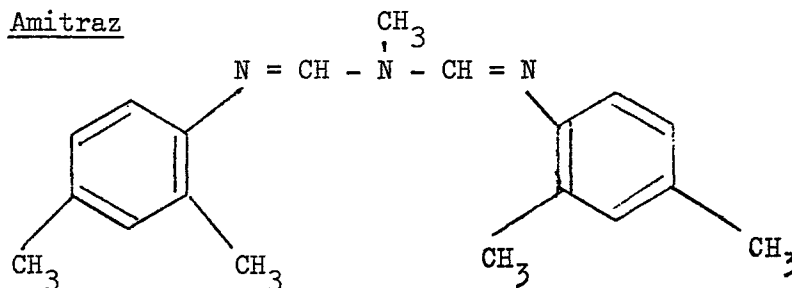
Thus, the joint action of two pesticides was analyzed by determining the actual toxicity indices of the components and of mixtures of the compounds by reference to dosage-mortality curves. The theoretical toxicity of the mixture is equal to the sum over both components of the percentage of each individual compound multiplied by its respective toxicity index. Therefore, the joint toxicity or co-toxicity coefficient of a mixture

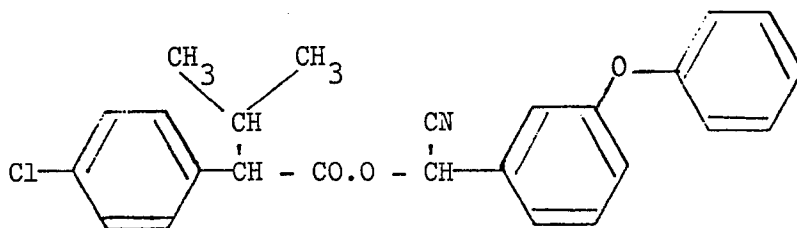
$$= \frac{\text{Actual toxicity index of a mixture}}{\text{Theoretical toxicity index of a mixture}} \times 100$$

A coefficient of a mixture near 100 indicates probability of similar action by the two pesticides; independent action usually should give a coefficient less than 100, while a coefficient significantly above 100 strongly indicates synergism.

The compounds tested in the Example are shown below.

Amitraz



Compound YEXAMPLEActivity of Pyrethroid/Amitraz mixture against Tetranychus urticae (glasshouse red spider mite)

5 The acaricidal activity of amitraz, compound Y and their mixtures was assessed by the following method.

The compounds and mixtures were formulated as solutions or suspensions in water containing 20% by weight of acetone and 0.05% by weight of Triton X-100 (Trade Mark) as wetting agent. The formulations contained 0.4% by weight of the compound or mixture to be tested and were diluted to produce formulations containing various concentrations. Leaf discs cut from French bean plants were sprayed with the formulations and left for $\frac{1}{2}$ to 1 hour drying period. Each leaf disc was then inoculated with 10 red spider mites and mortality counts made 24 hours after inoculation. From these results the LC_{50} 's (the concentration by weight of active material in the spray required to kill 50% of the mite population) could be calculated.

The toxicity indices of the compounds and the mixtures were calculated using the following formula:

$$20 \quad \text{Toxicity Index} = \frac{LC_{50} \text{ of amitraz}}{LC_{50} \text{ of compound or mixture}}$$

The coefficient of cotoxicities were then calculated according to the method described above. The results are shown in the following Table.

TABLE

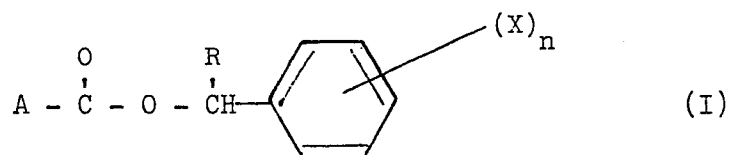
ACTIVITY OF PYRETHROID MIXTURES AGAINST THE
GLASSHOUSE RED SPIDER MITE (TETRANYCHUS URTICAE)

Treatment	Replicates		Coefficient of co- toxicity Replicates	
	1	2	1	2
Amitraz	0.12	0.14	-	-
Compound Y	0.40	0.36	-	-
Compound Y + Amitraz (2:1 ratio)	0.17	0.17	133	141

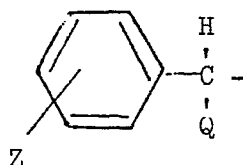
It will be seen that the coefficients of cototoxicity are both in excess of 100 and clearly demonstrate the synergistic effect of the amitraz/pyrethroid mixture.

C L A I M S

1. A pesticidal composition which comprises N,N-di(2,4-xylylaminomethyl)-methylamine, characterized in that the composition includes a pyrethroid insecticide having the general formula:



- 5 wherein A is an optionally-substituted aralkyl, alkyl or cycloalkyl group, R is hydrogen, cyano or ethynyl; X is alkyl, alkenyl, aralkyl or aryloxy and n is 1 to 5.
2. A composition according to claim 1, characterized in that in the compound of the general formula I, any alkyl, cyclo-
 10 alkyl or alkenyl group represented by A or X has up to 6 carbon atoms, and any aralkyl or aryloxy group represented by A or X has up to 10 carbon atoms.
3. A composition according to claim 1 or claim 2, characterized in that A represents an optionally-substituted aralkyl
 15 group.
4. A composition according to claim 3, characterized in that A represents a substituted benzyl group of the general formula:

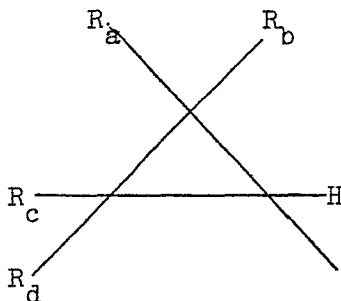


wherein Z represents a halogen atom or an alkoxy group having from 1 to 4 carbon atoms, and Q represents an alkyl group having from 1 to 6 carbon atoms.

5 A composition according to claim 4, characterized in that A represents an alpha-isopropyl-4-chlorobenzyl group, R represents a hydrogen atom or a cyano group, n represents 1 and X represents a 3-phenoxy group.

6. A composition according to claim 5, characterized in that the compound of the general formule I is alpha-cyano-3-phenoxy-
10 benzyl 2-(4-chlorophenyl)-3-methylbutanoate.

7. A compound according to claim 1 or claim 2, characterized in that A represents a cyclopropyl group of formula:



wherein R_a and R_b each individually represent an alkyl group having from 1 to 6 carbon atoms, or a halogen atom; or R_a and R_b together represent an alkylene group having from 2 to 6
15 carbon atoms; or R_a represents a hydrogen atom and R_b represents an alkenyl group having from 2 to 6 carbon atoms and from 1 to 3 chlorine or bromine atoms; R_c and R_d both represent an alkyl group having 1 to 6 carbon atoms, or R_c and R_d together re-
20 present an alkylene group having from 2 to 6 carbon atoms.

8. A method of combating pests at a locus, characterized in that a composition as claimed in any one of claims 1 to 7 is applied to the locus.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
P	NL - A - 70 18036 (BOOTS) * Claim 1; page 9, line 21 * --	1	A 01_N 9/02 C 07 C 87/00
	NL - A - 76 08375 (CIBA-GEIGY) * Claims 1,16; page 3, lines 30-36 * --	1	
	FR - A - 2 340 925 (CIBA-GEIGY) * Claims 1,19; page 4, line 5 * --	1	TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
	A	NL - A - 73 07130 (NATIONAL RESEARCH DEVELOPMENT CORP.) * Claims 28-32 * ----	1
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search The Hague		Date of completion of the search 23-11-1978	Examiner NATUS