

PATENT SPECIFICATION

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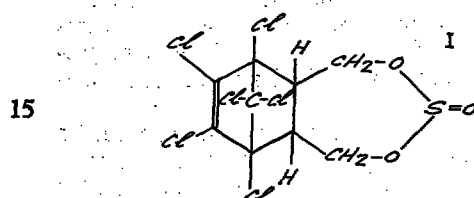
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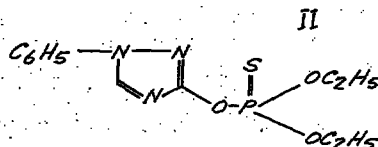
(54) PESTICIDES

(71) We, FARBWERKE HOECHST AKTIEN-GESELLSCHAFT, vormals Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to pesticidal compositions containing 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis-[hydroxymethylene - (5,6)] - sulphite of the following formula I



in admixture with 1 - phenyl - 3 - (O,O-diethylthionophosphoryl) - 1,2,4 - triazol of the following formula II



20 The hexachlorobicycloheptene compound of formula I is known from German Patent 1,015,797 and U.S. Patent 2,799,685. It is used as a pesticide, especially for combating biting and sucking insects in fruit and vegetable growing and in arable farming, and for combating beetles, caterpillars and scale insects in forestry.

It has been found, however, that the action of the said hexachlorobicycloheptene com-
 [Price 25p]

30 pound is not sufficient in special cases to completely destroy pests.

The present invention is based on the observation that mixtures of hexachlorobicyclo-[2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite with 1 - phenyl-3 - (O,O - diethylthionophosphoryl) - 1,2,4-triazol have an excellent action, especially in cases where the compound of formula I is inadequate. It is advantageous to use pesticides containing 1 to 10 parts by weight of hexachlorobicyclo - [2,2,1-] - heptene - (2) - bis-[hydroxymethylene - (5,6)] - sulphite in admixture with 1 part by weight of 1 - phenyl-3 - (O,O - diethylthionophosphoryl) - 1,2,4-triazol.

According to the invention, the mixtures of said active substances enable a large number of pests to be controlled far more effectively than when using the known hexachlorobicycloheptene compound alone. This fact is especially true for spider mites (*Tetranychidae*), scale insects (varieties or *Pseudococcus*), caterpillars of the family of the leaf-roller moths (*Tortricidae*) and pests that are difficult to control, for example, the Egyptian cotton leaf worm (*Prodenia litura* F.). It should be noted that the mixtures containing said active substances of formulae I and II show a synergistic effect, for example, in the control of the Mexican bean beetle (*Epilachna varivestis*). In addition to having a considerably improved insecticidal action in comparison with the individual components, the mixtures also show an ovicidal, acaricidal and nematocidal action.

The mixtures of active substances according to the invention may be made into wettable powders, emulsions, suspensions, dusting powders, granules, fly-bands, products for spreading and lotions using liquid or solid inert carriers, adhesives, wetting agents, dispersing agents or grinding auxiliaries. They can be mixed with other insecticides, fungicides, nematocides and herbicides.

As solid carrier materials, mineral substances may be used, for example: aluminium silicates, argillaceous earths, kaolin, chalks, siliceous

chalks, talcum, kieselguhr or hydrated silicic acids, or blends of these mineral substances together with special additives, for example chalk with sodium stearate.

5 As liquid carrier materials, there may be used all common and suitable organic solvents, for example, ketones, for example, methyl ethyl ketone, methyl isobutyl ketone and isophorone; esters, for example butyl acetate and glycol diacetate; ethers, for example, diethylene glycol dimethyl ether, diethylene glycol diethyl ether and diethylene glycol dibutyl ether, and high boiling aromatic substances, for example, xylene, anisole, decalin and tetralin.

15 Suitable adhesives are glutinous cellulose products or polyvinyl alcohols.

As wetting agents, any suitable emulsifier may be used, for example, oxyethylated alkyl phenols, fat alcohol polyglycol ethers, fatty acid polyglycol esters, salts or aryl- or alkyl-aryl-sulphonic acids, salts of methyl taurine, salts of oxyethylated phenyl sulphonic acids, or soaps.

20 Suitable dispersing agents are cell pitch (salts of lignin-sulphonic acid), salts of naphthalene-sulphonic acid and, in special cases, hydrated silicic acids or kieselguhr.

As grinding auxiliaries, there may be used suitable organic or inorganic salts, for example, sodium sulphate, ammonium sulphate, sodium carbonate, sodium bicarbonate, sodium thiosulphate, sodium stearate or sodium acetate.

25 The pesticidal compositions of the invention advantageously contain 10 to 70% by weight of a mixture of active substances and 5 to 15% by weight of a wetting agent, while the remaining proportion of the total amount of 100% by weight i.e. 85 to 15% by weight, is made up by a solid or liquid carrier material.

30 In the so-called ultra-low-volume process, where highly concentrated mixtures are sprayed through nozzles from airplanes, pesticides may be used which contain 70 to 95% by weight of a mixture of active substances in accordance with the invention, and 30 to 5% by weight of aliphatic and/or aromatic mineral oils and/or ketones, the said mineral oils or ketones having boiling points above 120°C, and/or vegetable oils, for example, cotton seed oil or 35 castor oil, and/or liquid emulsifiers, for

example, oxyethylated alkyl phenols, for example, nonyl phenol, with 5 to 15 ethylene oxide units in the molecule.

The following Examples illustrate the invention, the percentages being by weight.

EXAMPLE 1

55 A xylene solution containing 35% of 1,2,3,4,7,7-hexachlorobicyclo-[2,2,1]-heptene-(2)-bis-[hydroxymethylene-(5,6)]-sulphite (A) and 6% of an emulsifier mixture composed of alkylaryl sulphonates and ethoxylated alkyl phenols, was emulsified in water together with a xylene solution containing 40% of 1-phenyl-3-(O,O-diethylthionophosphoryl)-1,2,4-triazol (B), 10% of an emulsifier mixture of alkylaryl sulphonates with ethoxylated alkyl phenols, and 2% fatty acid polyglycol ester, in a manner such that the concentration of active substance of the bicycloheptene derivative (A) was 0.007% or 0.0035% and the concentration of active substance of the triazol derivative (B) was 0.001% or 0.0005%.

Using this mixture of active substances in accordance with the invention, equal proportions were mechanically measured out in order to spray Mexican bean beetles (*Epilachna varivestis* Muls.) in the stages of larva and imago, respectively, as well as their food consisting of Phaseolus leaves, with equal amounts of active substances per unit area. After treatment, the animals were placed on the dried leaves. The action of the mixture of active substances was determined after 1, 2, 3 and 5 days, respectively. The results are indicated in the following Table I.

60 In a comparison test, Mexican bean beetles were treated under the same conditions with the above bicycloheptene derivative (A) in the above xylene solution emulsified in water to obtain a concentration of active substance of 0.007% and 0.0035%, respectively. This comparison is designated in Table I as "Comp. I".

65 In another comparison test, Mexican bean beetles were treated under the same conditions with the above triazol derivative (B) in the above xylene solution emulsified in water to obtain a concentration of active substance of 0.001% and 0.0005%, respectively. This comparison is indicated in Table I as "Comp. II".

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TABLE I

Active substance	Concentration of active substance	Beetles killed (damaged) in per cent			
		after 1	2	3	5 days
mixture of active substances of the invention Comp. I Comp. II	(0.007% A)	100 (0)			
	(0.001% B)	0 (0)	0 (0)	0 (0)	0 (0)
	0.007% A 0.001% B	20 (10)	40 (0)	40 (0)	40 (0)
		Larvae killed (damaged) in per cent			
		after 1	2	3	5 days
mixture of active substances of the invention Comp. I Comp. II	(0.0035% A)	0 (100)	40 (60)	80 (20)	100 (0)
	(0.0005% B)	0 (0)	0 (0)	0 (0)	0 (0)
	0.0035% A 0.0005% B	0 (10)	10 (20)	30 (0)	30 (0)

According to Table I, the beetles were completely killed after 1 day by the mixture of active substances of the invention used in the test I, there was no effect even after 5 days and in comparison test II, only 40% of the beetles had been killed after 2 or more days. The larvae were damaged to an extent of 100% after 1 day by the mixture of active substances in accordance with the invention, used in the indicated concentration (which was half the concentration used for the beetles), whereas comparison test I showed no effect and in comparison test II, only 30% of the larvae

had been killed after 5 days. When carrying out the tests, it was further found that the leaves treated with the mixture of active substances in accordance with the invention were only gnawed at in traces by the beetles, so that the plants were, in effect, undamaged, whereas the leaves treated with the comparison emulsions were either completely destroyed or destroyed to a large extent by the beetles.

EXAMPLE 2

Apples of the size of a walnut were sprayed on all sides with a mixture of active substances in accordance with the invention having a

composition analogous to that of Example 1, and containing 0.2% of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite (A) and 0.025% 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol (B) in an aqueous emulsion.

The apples were dried while suspended from their stalks, and eggs of the codling moth (*Carpocapsa pomonella* L.) were then placed thereon. The evaluation after 7 days showed that 100% of the hatched caterpillars had been killed.

In a comparison test, only 52% of the hatched caterpillars was killed by treatment with an emulsion containing 0.2% of substance (A), under otherwise the same conditions.

In another comparison test using an emulsion containing 0.025% of substance (B), only 88% of the hatched caterpillars was killed under otherwise the same conditions.

EXAMPLE 3

Small apple trees in pots, which trees had been strongly infested with European red mites (*Metatetranychus ulmi* Koch) were sprayed with a mixture of active substances in accordance with the invention having a composition analogous to that of Example 1, and containing 0.04% of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxy-

methylene - (5,6)] - sulphite (A) and 0.01% 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol (B). When the acaricidal and ovicidal action was determined after 8 days by microscopic counting, a 100% destruction of the red mites and eggs was found.

EXAMPLE 4

Small mandarin trees in pots, which trees were strongly infested with scale insects, Citrus mealy bug (*Pseudococcus citri* Risso) were sprayed with a mixture of active substances in accordance with the invention having a composition analogous to that of Example 1 and containing 0.04% of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite (A) and 0.02% 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol (B). The mealy bugs were completely destroyed within 4 days.

EXAMPLE 5

In addition to the mixtures of active substances according to the invention as described in Example 1, the mixtures of active substances indicated in the following Table II may, for example, also advantageously be used. These emulsion concentrates were emulsified in a corresponding amount of water to obtain the desired concentrations of active substance.

TABLE II

	a)	b)	c)
active substance (A)	20%	30%	35%
active substance (B)	5%	30%	5%
calcium alkylphenylsulphonate	4.7%	6%	6.5%
fatty acid polyglycol ester	11%	9%	14%
xylene	59.3%	25%	39.5%

WHAT WE CLAIM IS:—

1. A pesticidal composition, which comprises 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite in admixture with 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol.

2. A pesticidal composition as claimed in claim 1, wherein there is also present one or more of the following:—a liquid or solid carrier, an adhesive, a wetting agent, a dispersing agent, a grinding auxiliary and/or other insecticides, fungicides, nematocides and herbicides.

3. A pesticidal composition as claimed in

claim 1 or 2, wherein there is present 1 to 10 parts by weight of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite in admixture with 1 part by weight of 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol.

4. A pesticidal composition as claimed in any one of claims 1 to 3, wherein there is present 10 to 70% by weight of a mixture of the active substances in admixture with 5 to 15% by weight of a wetting agent and 85 to 15% by weight of a solid or liquid carrier material.

5. A pesticidal composition as claimed in

composition analogous to that of Example 1, and containing 0.2% of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite (A) and 0.025% 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol (B) in an aqueous emulsion.

The apples were dried while suspended from their stalks, and eggs of the codling moth (*Carpocapsa pomonella* L.) were then placed thereon. The evaluation after 7 days showed that 100% of the hatched caterpillars had been killed.

In a comparison test, only 52% of the hatched caterpillars was killed by treatment with an emulsion containing 0.2% of substance (A), under otherwise the same conditions.

In another comparison test using an emulsion containing 0.025% of substance (B), only 88% of the hatched caterpillars was killed under otherwise the same conditions.

EXAMPLE 3

Small apple trees in pots, which trees had been strongly infested with European red mites (*Metatetranychus ulmi* Koch) were sprayed with a mixture of active substances in accordance with the invention having a composition analogous to that of Example 1, and containing 0.04% of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxy-

methylene - (5,6)] - sulphite (A) and 0.01% 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol (B). When the acaricidal and ovicidal action was determined after 8 days by microscopic counting, a 100% destruction of the red mites and eggs was found.

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Small mandarin trees in pots, which trees were strongly infested with scale insects, Citrus mealy bug (*Pseudococcus citri* Risso) were sprayed with a mixture of active substances in accordance with the invention having a composition analogous to that of Example 1 and containing 0.04% of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite (A) and 0.02% 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol (B). The mealy bugs were completely destroyed within 4 days.

EXAMPLE 5

In addition to the mixtures of active substances according to the invention as described in Example 1, the mixtures of active substances indicated in the following Table II may, for example, also advantageously be used. These emulsion concentrates were emulsified in a corresponding amount of water to obtain the desired concentrations of active substance.

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xylene	59.3%	25%	39.5%

WHAT WE CLAIM IS:—

1. A pesticidal composition, which comprises 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite in admixture with 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol.

2. A pesticidal composition as claimed in claim 1, wherein there is also present one or more of the following:—a liquid or solid carrier, an adhesive, a wetting agent, a dispersing agent, a grinding auxiliary and/or other insecticides, fungicides, nematocides and herbicides.

3. A pesticidal composition as claimed in

claim 1 or 2, wherein there is present 1 to 10 parts by weight of 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1] - heptene - (2) - bis - [hydroxymethylene - (5,6)] - sulphite in admixture with 1 part by weight of 1 - phenyl - 3 - (O,O - diethylthionophosphoryl) - 1,2,4 - triazol.

4. A pesticidal composition as claimed in any one of claims 1 to 3, wherein there is present 10 to 70% by weight of a mixture of the active substances in admixture with 5 to 15% by weight of a wetting agent and 85 to 15% by weight of a solid or liquid carrier material.

5. A pesticidal composition as claimed in



5 any one of claims 2 to 4, wherein the solid carrier material is aluminium silicate, argillaceous earth, kaolin, chalk, siliceous chalk, talc, kieselguhr or hydrated silicic acid.

5 6. A pesticidal composition as claimed in any one of claims 2 to 4, wherein the liquid carrier material is an organic solvent.

7. A pesticidal composition as claimed in claim 6, wherein the liquid carrier material is a ketone, an ester and/or a high boiling aromatic substance.

10 8. A pesticidal composition as claimed in any one of claims 2 to 7, wherein as wetting agent there is present, an oxyethylated alkyl phenol, a fat alcohol polyglycol ether, a fatty acid polyglycol ester, a salt of an aryl- or alkylaryl-sulphonic acid, a salt of methyl taurine, a salt of an oxyethylated phenyl-sulphonic acid or a soap.

15 20 9. A pesticidal composition as claimed in any one of claims 2 to 8, wherein as dispersing agent there is present: a salt of lignin-

25 sulphonic acid, a salt of naphthalene-sulphonic acid, a hydrated silicic acid or kieselguhr.

10. A pesticidal composition as claimed in any one of claims 2 to 9, comprising 70—95% by weight of a mixture of the active substances 1,2,3,4,7,7 - hexachlorobicyclo - [2,2,1]-heptene - (2) - bis - [hydroxymethylene-(5,6)] - sulphite and 1 - phenyl - 3 - (O,O-diethyl thionophosphoryl) - 1,2,4 - triazol, in admixture with 30—5% by weight of aliphatic and/or aromatic mineral oils or ketones boiling above 120°C.

11. A pesticidal composition as claimed in claim 1, and substantially as described in any one of Examples 1 to 5 herein.

12. A method of controlling pests, which comprises applying to the pests a composition as claimed in claim 1.

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