

PATENT SPECIFICATION

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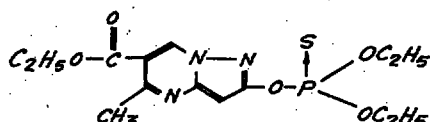
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 1C5H 1C5J 1C5R 1C6A2B 1C6B



(54) PESTICIDALLY ACTIVE MIXTURES AND COMPOSITIONS CONTAINING THEM

(71) We, HOECHST AKTIEN-GESELLSCHAFT formerly known as Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, a body corporate recognised under German Law, of 6230 Frankfurt (Main) 80, Federal Republic of 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:—

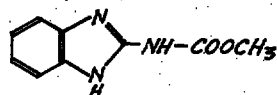
This invention relates to pesticidally active mixtures and to compositions containing them. The present invention provides a pesticidally active mixture of 2-(O,O-diethyl-thiono-phosphoryl) - 5 - methyl - 6 - carbethoxy-pyrazolo-(1,5-a)-pyrimidine of the formula



(I)

with

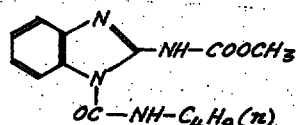
(a) 2 - methoxycarbonylamino - benzimidazole of the formula



(II)

or

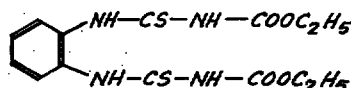
(b) 1 - (N - butylcarbamoyl) - 2-methoxycarbonyl-amino-benzimidazole of the formula



(III)

or

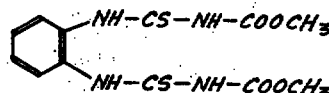
(c) 1,2 - bis(3 - ethoxycarbonyl - 2-thioureido)-benzene of the formula



(IV)

or

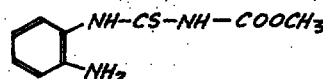
(d) 1,2 - bis(3 - methoxycarbonyl - 2-thioureido)-benzene of the formula



(V)

or

(e) 1 - (3 - methoxycarbonyl - 2-thioureido)-2-aminobenzene of the formula



(VI)

The compound of the formula (I) is known from German Patent No. 1,545,790 and is used as a fungicide, mainly against mildew. The compounds of formulae (II) to (VI), as well as their fungicidal effects, are also known (II: U.S. Patent No. 3,010,968; III: Netherlands Specification No. 6,706,331; IV and V: German Offenlegungsschrift No. 1,806,123; Japanese Patent No. 638,021).

It has now been found that mixtures of compound (I) with compounds (II), (III), (IV), (V) and (VI), respectively, have not only an additive but also a synergistic effect against phytopathogenic fungi. The synergistic effect is observed with mixtures in weight ratios in the range of from 10:1 to 1:10, especially 5:1 to 1:5.

With the mixtures of compounds according

to the present invention the same pesticidal effect as obtained with the individual components can be achieved with lower concentrations. Moreover, the danger of resistance, as observed with the use of benzimidazole compounds, is considerably reduced with the mixtures of the present invention.

The mixtures of the present invention can be used successfully against a plurality of phytopathogenic fungi, especially against genuine mildew, as well as against *ascomycetes* and *fungi imperfecti*. By way of example, the following may be named: *Venturia inaequalis* causing apple scab, *Podosphaera leucotricha* causing apple mildew and *Botrytis cinerea* causing botrytis disease in fruit.

When applied in suitable dosage, the mixtures of the present invention have a protective as well as a curative effect. They are especially suitable for combating or preventing fungus diseases in living plants, for example in orchards and nurseries, ornamental plants, vegetables, shrubs, cereals, salad plants and potatoes.

The mixtures of the present invention can be applied in the form of for example, wettable powders, dusting powders, granules and advantageously in the form of dispersions.

The present invention therefore also provides a pesticidal composition comprising as active ingredient, a mixture as described above, together with one or more formulation auxiliaries.

The present invention further provides a method for combating phytopathogenic fungi which comprises applying to the locus of plants infested therewith a mixture or composition according to the present invention.

Dispersions may be formed by dispersing from 10 to 40% by weight of the active mixture in a high boiling liquid organic medium, for example in paraffinic or vegetable oils or higher boiling liquid organic dispersion media such as ethers and liquid esters of organic mono- and dicarboxylic acids and aliphatic alcohols having from 8 to 18 carbon atoms, preferably phthalic acid esters, for example phthalic acid diisooctyl ester. The compound (I) is suitably incorporated into the dispersions as a solution in an aromatic solvent.

In the preparation of wettable powders and dusts the compound I is first adsorbed on finely dispersed carrier materials, such as synthetic silicic acids, diatomaceous earth, or bentonites, and then ground together with one of the compounds (II) to (VI), a further amount of carrier material and dispersing agents, wetting agents and adhesives. In the preparation of dusts, talc or calcium silicates and clays are expediently used as carrier materials.

Granules are preferably prepared by impregnating an inert granular carrier material, for example quartz sand, with a solu-

tion of compound (I) in a high boiling solvent, for example high boiling fractions of aromatic hydrocarbons, ketones, for example isophorone, advantageously in the presence of an emulsifier and a stabilizer, and applying onto the wetted sand one of the compounds (II) to (VI) in finely ground form, while drying the granules. Alternatively, a solution of the compound (I) is applied to an absorbent granular carrier material, for example attapulgit, and a ground powder of one of the compounds (II) to (VI) is applied onto the said granules.

Suitable dispersing agents for the wettable powders are the sodium salts of dinaphthyl-methane-disulfonic acid, of dialkyl-naphthalene-sulfonic acids, of oleylmethyl-tauride as well as alkali metal and alkaline earth metal salts of lignin-sulfonic acids, or sodium salts of sulfosuccinic acid esters. Suitable wetting agents are sodium dodecyl-benzenesulfonates or polyethylene or polypropylene glycols adsorbed on synthetic silicic acids. Suitable adhesives are partially saponified polyvinyl acetates, polyvinyl alcohols, polyvinyl-pyrrolidones, carboxyethyl cellulose, hydroxyethyl cellulose, as well as vegetable gums.

The following organic dispersion media are suitable for the formulation of liquid dispersions: O-acyl- and nonyl-phenol polyglycol ethers, triisobutyl-phenol polyglycol ether, castor oil polyglycol ethers or esters, preferably in the presence of a calcium salt of dodecyl-benzenesulfonic acid. Depending on the chain length of the polyglycol ethers or esters, these substances are more or less suitable as dispersion agents in paraffin oils, vegetable oils or other organic liquid dispersion media.

Owing to the high boiling point of the organic dispersion media the dispersions are well suitable for an application according to the ultra-low-volume process, the more so as the formulations can easily be diluted with water or further organic liquids, such as fractions of paraffin oils, without the active ingredient flocculating.

To ensure a satisfactory handling and good fluidity of the dispersions, they contain of from 10 to 40% by weight, preferably 20 to 25% by weight of the mixture of active ingredients. Wettable powders may contain up to 70% by weight, granules 2 to 20% by weight and dusts 2 to 10% by weight of the mixture of active ingredients.

The following Examples illustrate the invention. The words 'MOBIL' and 'MOBILSOL' used in the Examples are registered Trade Marks.

EXAMPLE 1:

A dispersion in paraffin oil is obtained by finely grinding in a grinding ball mill:

5

10

15

20

25

30

35

40

45

50

55

60

65

70

75

80

85

90

95

100

105

110

115

120

125

15.0% by weight of active compound II
 3.0% by weight of active compound I
 0.07% by weight of epichlorohydrin
 7.50% by weight of nonyl-phenol polyglycol ether
 3.25% by weight of triisobutyl-phenol polyglycol ether
 2.65% by weight of calcium dodecylbenzenesulfonate
 0.70% by weight of ricinol polyglycol ether or ester
 8.33% by weight of xylene
 59.50% by weight of paraffin oil.

EXAMPLE 2:

A wettable powder is composed of:

30.0% by weight of active compound II
 15.0% by weight of active compound I
 7.5% by weight of paraffin-containing aromatic oil (Mobilsol® F of Mobil Oil AG)
 37.0% by weight of finely dispersed silicic acid
 5.0% by weight of sodium dinaphthalene-disulfonate
 2.0% by weight of sodium dibutyl-naphthalene-disulfonate
 0.5% by weight of epichlorohydrin
 2.0% by weight of partially saponified polyvinyl acetate
 1.0% by weight of polypropylene glycol.

EXAMPLE 3:

A granular composition containing 5.75% by weight of total active ingredients is obtained as follows:

91.275% by weight of quartz sand (particle size 0.3 to 1 mm) are wetted with a solution of 0.75% by weight of active compound I in 0.75% by weight of aromatic oil (Mobilsol F Mobil Oil AG) and 0.025% by weight of epichlorohydrin.

In a mixer 7.20% by weight of a finely ground mixture of 70% by weight of active compound II with silicic acid is applied by rolling onto the wet sand.

EXAMPLE 4:

As comparative composition a 50% by weight wettable powder of active compound II is prepared as follows:

50% by weight of active compound II
 5% by weight of sodium dinaphthyl-methane-disulfonate
 2% by weight of sodium dibutyl-naphthalene-sulfonate
 2% by weight of partially saponified polyvinyl acetate
 1% by weight of polypropylene glycol
 19% by weight of powdered skim milk
 21% by weight of synthetic finely dispersed silicic acid.

EXAMPLE 5:

As comparative composition a 30% by weight emulsion concentrate of active compound I is prepared from:

30% by weight of active compound I
 5.5% by weight of ricinol-polyglycol ether
 4.5% by weight of calcium phenyl sulfonate
 0.5% by weight of epichlorohydrin
 59.5% by weight of xylene.

EXAMPLE I:

Cucumber plants grown in pots in the greenhouse were strongly infested in the two-leaf stage with a suspension of conidia of cucumber mildew (*Erysiphe cichoracearum* D.C.) and kept for one day in a moisture chamber at 95—100% of relative atmospheric humidity and at 20° C. Next, the plants were placed in the greenhouse at a temperature of 22° C and, after a period of 5 days, the infested plants were treated with combinations of active compounds I and II as specified in Table I. Care was taken that the leaves were well wetted. After drying of the layer of spray liquor the plants were again placed in the greenhouse and, after an incubation time, they were kept under observation until the untreated control plants showed a distinct layer of mildew. The degree of infestation with mildew was evaluated by visual inspection. The degree of infestation was ascertained according to the scheme of numbers 1 to 9 drawn up by the "Biologische Bundesanstalt in Braunschweig" (BBA), Federal Republic of Germany (see below). The synergistic effect of the combination of active compounds was evaluated by the method according to Horsfall or Sakai (cf. J. G. Horsfall "Fungicides and their action" *Chronica Botanica*, 1945, (Walham, Mass.), pages 239 et seq; Sakai et al. "Insect Toxicological Studies in the Joint Toxic Action of Insecticides between Contact Insecticides" *Boty-Kagaku*, 16 (1951), pages 130—140).

EXAMPLE II:

In the manner described in Example I tests were carried out with mixtures of active compound I with compounds III, IV, V, and VI respectively. The results are indicated in the following Tables II to V.

BBA Scheme: degree of efficiency
 (% of non infested
 leaf surface)

1	100%
2	97.5%
3	95%
4	90%
5	85%
6	75%
7	65%
8	32.5%
9	0%

In the Tables, percentages are by weight.

TABLE I

Concentration applied		active compound I 30% emulsion concentrate	+	active compound II 50% wetable powder	evaluated according to BBA scheme	average	efficiency % of non-infested leaf surface
					6 repetitions		
0				0.003 %	6 6 7 8 6 7	6.6	70
0.0006	%		+	0.0024 %	5 5 3 4 3 3	3.8	92
0.0012	%		+	0.0018 %	2 3 2 2 3 3	2.5	96
0.0018	%		+	0.0012 %	4 3 2 3 3 3	3.0	95
0.0024	%		+	0.0006 %	5 4 4 5 5 4	4.5	88
0.003	%			—	5 5 6 5 6 6	5.5	80
untreated					9 9 9 9 9 9	9	0

TABLE II

Concentration applied		Compound I 30% emulsion concentrate	+	Compound III 50% wetable powder	evaluated according to BBA scheme	average	efficiency (% of non-infested leaf surface)
					6 repetitions		
0				0.003 %	5 5 6 6 5 4	5.2	81
0.0006	%		+	0.0024 %	3 3 4 3 3 3	3.2	94
0.0012	%		+	0.0018 %	2 2 3 3 2 3	2.5	96
0.0018	%		+	0.0012 %	3 3 2 3 2 2	2.5	96
0.0024	%		+	0.0006 %	4 5 4 5 5 4	4.5	87
0.003	%				5 6 5 5 5 6	5.4	80
untreated					9 9 9 9 9 9	9.0	0

TABLE III

Compound I 30 % emulsion concentrate	+	Compound IV 50 % wetable powder	evaluated according to BBA scheme 4 repetitions	average
		0.003 %	5 6 5 5	5.25
0.0006	+	0.0024	4 3 4 4	3.75
0.0012	+	0.0018	3 4 2 3	3.00
0.0018	+	0.0012	5 5 5 5	5.00
0.0024	+	0.0006	6 6 5 6	5.75
0.003			7 6 6 7	6.5
untreated			9 9 9 9	9

TABLE IV

Compound I 30 % emulsion concentrate	+	Compound V 70 % wetable powder	evaluated according to BBA scheme 4 repetitions	average
		0.003	3 2 2 3	2.25
0.0006	+	0.0024	1 1 1 1	1.0
0.0012	+	0.0018	2 3 2 3	2.25
0.0018	+	0.0012	3 4 3 3	3.25
0.0024	+	0.0006	4 5 5 4	4.50
0.003			7 6 6 7	6.50
untreated			9 9 9 9	9.0

TABLE V

Compound I 30 % emulsion concentrate	+	Compound VI 50 % wetable powder	evaluated according to BBA scheme 4 repetitions	average
		0.003	3 3 3 3	3.0
0.0006	+	0.0024	2 1 1 1	1.25
0.0012	+	0.0018	2 3 2 2	2.25
0.0018	+	0.0012	3 4 3 4	3.5
0.0024	+	0.0006	4 5 5 4	4.5
0.003			7 6 6 7	6.5
untreated			9 9 9 9	9

EXAMPLE IV.

Apple trees of the variety Jonathan were sprayed against apple scab (*Podosphaera leucotricha* Salm.) ten times at intervals of 14 days each with a mixture of 1 part of active compound I and 2 parts of active compound II in a total concentration of 0.04% by weight, with the individual compounds each in a concentration of 0.04% by weight and, for comparison, with 0.05% by weight of

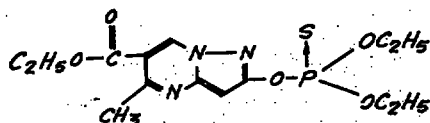
binapacryl (4,6 - dinitro - 2,6 - butylphenyl-beta-dimethyl acrylate). For each spraying about 2000 l/ha of spray liquor were used. At the end of the vegetation period in late autumn the number of infested shoot ends was counted. In Table VI is given the percentage of mildew infested terminal buds of a total number of 200 shoot ends for each tree.

TABLE VI

	concentration of active compound	infestation of shoot ends %
untreated	—	56
active compound I	0.04 %	20
active compound II	0.04 %	24
active compound I + active compound II (ratio 1:3)	0.04 %	14
binapacryl	0.05 %	20

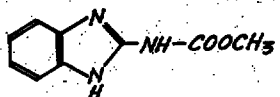
WHAT WE CLAIM IS:—

1. A pesticidally active mixture of 2-(O,O-diethyl - thiono - phosphoryl) - 5 - methyl-6 - carbethoxy - pyrazolo - (1,5-a) - pyrimidine of the formula



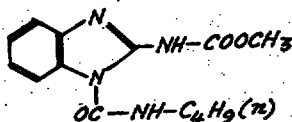
with

(a) 2 - methoxycarbonylamino - benzimidazole of the formula



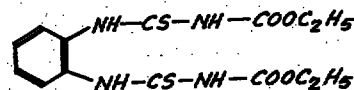
or

(b) 1 - (N - butylcarbamoyl) - 2-methoxycarbonyl - amino - benzimidazole of the formula



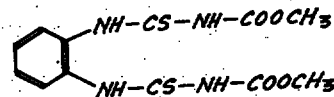
or

(c) 1,2 - bis(3 - ethoxycarbonyl - 2-thioureido)-benzene of the formula



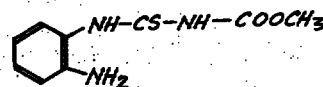
or

(d) 1,2 - bis - (3 - methoxycarbonyl - 2-thioureido)-benzene of the formula



or

(e) 1 - (3 - methoxycarbonyl - 2-thioureido)-2-aminobenzene of the formula VI



2. A mixture as claimed in claim 1, containing the two components in a weight ratio of from 10:1 to 1:10.

3. A mixture as claimed in claim 2, containing the two components in a weight ratio of from 5:1 to 1:5.

EXAMPLE IV.

Apple trees of the variety Jonathan were sprayed against apple scab (*Podosphaera leucotricha* Salm.) ten times at intervals of 14 days each with a mixture of 1 part of active compound I and 2 parts of active compound II in a total concentration of 0.04% by weight, with the individual compounds each in a concentration of 0.04% by weight and, for comparison, with 0.05% by weight of

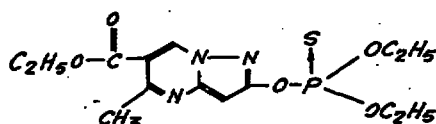
binapacryl (4,6 - dinitro - 2,6 - butylphenyl-beta-dimethyl acrylate). For each spraying about 2000 l/ha of spray liquor were used. At the end of the vegetation period in late autumn the number of infested shoot ends was counted. In Table VI is given the percentage of mildew infested terminal buds of a total number of 200 shoot ends for each tree.

TABLE VI

	concentration of active compound	infestation of shoot ends %
untreated	—	56
active compound I	0.04 %	20
active compound II	0.04 %	24
active compound I + active compound II (ratio 1:3)	0.04 %	14
binapacryl	0.05 %	20

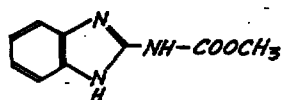
WHAT WE CLAIM IS:—

1. A pesticidally active mixture of 2-(O,O-diethyl - thiono - phosphoryl) - 5 - methyl-6 - carbethoxy - pyrazolo - (1,5-a) - pyrimidine of the formula



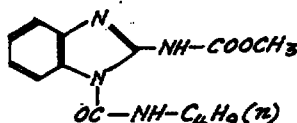
with

(a) 2 - methoxycarbonylamino - benzimidazole of the formula



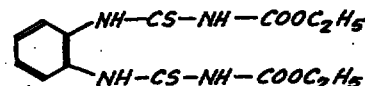
or

(b) 1 - (N - butylcarbamoyl) - 2 - methoxycarbonyl - amino - benzimidazole of the formula



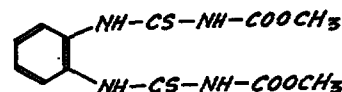
or

(c) 1,2 - bis(3 - ethoxycarbonyl - 2-thioureido)-benzene of the formula



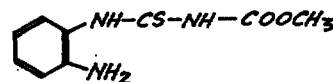
or

(d) 1,2 - bis - (3 - methoxycarbonyl - 2-thioureido)-benzene of the formula



or

(e) 1 - (3 - methoxycarbonyl - 2-thioureido)-2-aminobenzene of the formula VI



2. A mixture as claimed in claim 1, containing the two components in a weight ratio of from 10:1 to 1:10.

3. A mixture as claimed in claim 2, containing the two components in a weight ratio of from 5:1 to 1:5.



- 7
4. A pesticidal composition comprising as active ingredient a mixture as claimed in any of claims 1 to 3 together with one or more formulation auxiliaries.
5. A pesticidal composition as claimed in claim 4, containing from 2 to 70% by weight of the active ingredient mixture.
6. A pesticidal composition as claimed in claim 4 or claim 5 containing from 10 to 40% by weight of the active ingredient mixture in dispersion in a high boiling liquid organic medium.
7. A pesticidal composition as claimed in claim 6, containing the active ingredient mixture in dispersion in a paraffin oil, vegetable oil, ether or liquid of an organic mono- or dicarboxylic acid and an aliphatic alcohol having from 8 to 18 carbon atoms.
8. A pesticidal composition as claimed in claim 6 containing the active ingredient mixture in dispersion in phthalic acid diiso-octyl ester.
9. A pesticidal composition as claimed in claim 5 substantially as described in any one of Examples 1 to 3 herein.
10. A method for combating phytopathogenic fungi which comprises applying to the locus of plants infested therewith a mixture as claimed in claim 1 or a composition as claimed in claim 5.
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- 30
- ABEL & IMRAY,
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