

PATENT SPECIFICATION

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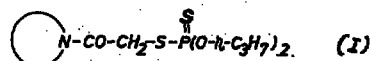
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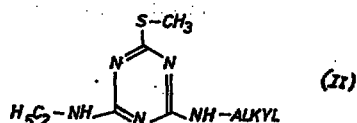
(54) SYNERGISTICALLY ACTIVE HERBICIDAL MIXTURES FOR THE CONTROL OF WEEDS IN RICE CROPS

(71) We, CIBA-GEIGY A.G. a body corporate, organised according to the laws of Switzerland, of 4002 Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

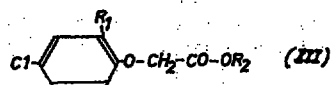
The present invention relates to synergistically active herbicidal mixtures of active substances for the control of weeds in rice crops, as well as to the use of the said synergistic herbicidal mixtures. The mixtures according to the invention comprise an active substance of formula I



wherein the N-containing ring represents a cyclohexamethyleneimine radical or the 2-methylpiperidyl group, and at least one active substance of formula II



wherein "alkyl" denotes a lower alkyl radical containing 2 to 5 carbon atoms, or at least one growth hormone of the phenoxyacetic acid type of formula III



wherein R₁ represents a chlorine atom or the methyl group, and R₂ represents hydrogen, an

alkali metal atom, or an alkyl radical containing 1 to 8 carbon atoms, preferably 1 to 4 carbon atoms.

The ratio of the mixture components I: II or I: III is 10:1 to 1:3, preferably 6:1 to 1:1 parts by weight.

Suitable alkyl radicals for the formula II are ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec. butyl, tert. butyl and all eight amyl isomers.

As alkyl radicals for the formula III there may be cited preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, hexyl, heptyl and isoctyl.

Particularly important mixture components of type II are:

- 2 - methylthio - 4 - ethylamino - 6 - isopropyl-amino - s - triazine, 45
- 2 - methylthio - 4 - ethylamino - 6 - sec. butyl-amino - s - triazine,
- 2 - methylthio - 4 - ethylamino - 6 - isobutylamino - s - triazine, 50
- 2 - methylthio - 4 - ethylamino - 6 - tert. butylamino - s - triazine,
- 2 - methylthio - 4 - ethylamino - 6 - [α,β-dimethylpropylamino] - s - triazine,
- 2 - methylthio - 4,6 - bis(ethylamino) - s - triazine. 55

Particularly important mixture components of type III are:

- 2,4-dichlorophenoxyacetic acid or the salts thereof, 60
- 2,4-dichlorophenoxyacetic acid ethyl ester,
- 2,4-dichlorophenoxyacetic acid methyl ester,
- 2,4-dichlorophenoxyacetic acid n-propyl ester,
- 2,4-dichlorophenoxyacetic acid isopropyl ester, 65
- 2,4-dichlorophenoxyacetic acid n-butyl ester,
- 2-methyl-4-chlorophenoxyacetic acid or the salts thereof,
- 2-methyl-4-chloro-phenoxyacetic acid isobutyl ester,
- 2-methyl-4-chloro-phenoxyacetic acid isoctyl ester, 70

- 2-methyl-4-chloro-phenoxyacetic acid ethyl ester,
 2-methyl-4-chloro-phenoxyacetic acid propyl ester
 5 2 - methyl - 4 - chloro - phenoxyacetic acid isopropyl ester,
 2 - methyl - 4 - chloro - phenoxyacetic acid n-butyl ester,
 10 2 - methyl - 4 - chloro - phenoxyacetic acid hexyl ester.

Dithiophosphates of formula I are known from the French Patent 1,594,966 or from the Indian Patent No. 118,938 as herbicides.
 15 1,3,5-Triazines of formula II and phenoxyacetic acid derivatives of formula III have been in use for a long time for the regulation of plant growth, particularly as herbicides.

It was not to be anticipated that dithiophosphates of formula I would develop a

- Alternanthera phyloxeroides
 Ammannia spp.
 Bidens sp.
 Boerhaavia erecta
 45 Callitriche sp.
 Cyperus compactus
 Cyperus difformis
 Cyperus diffusus
 Cyperus iria
 50 Cyperus microiria
 Cyperus serotinus
 Digitaria sanguinalis
 Dopatrium junceum
 Echinochloa colonum
 55 Echinochloa crus-galli
 Eclipta alba
 Elatine orientalis
 Elatine triandra
 Eleocharis acicularis
 60 Eleocharis atropurpureus
 Eriocaulon cinereum
 Eriocaulon sieboldianum
 Fimbristylis miliacea
 Ixophorus unisetus
 65 Leptochloa chinensis
 Leptochloa filiformis

The applied amounts of the active substance mixture can naturally vary depending on the mixture ratio and on the number of employed
 70 components I and II or I and III. The amounts are, in general, between 0.1 and 10 kg of active substance mixture per hectare, preferably 0.2 to 5 kg/hectare.

The active-substance mixtures may be used
 75 on their own, or together with one or more carriers or additives. Such carriers or additives can be either solid or liquid and take the form of solvents, diluents, dispersants, wetting agents, adhesives, thickeners or binders.
 80

The active substance mixtures are formulated accordingly as emulsion or suspension

synergistic action when used in admixture with active substances of formula II or formula III.

By synergism is meant in this connection an increased overall effect which exceeds, in the desired direction, the purely cumulative individual effects of the respective components concerned. In the following text the term is taken to include also the improvement in the sphere of action against weeds, the reduction or elimination of undesirable secondary effects of the active substances with respect either to cultivated plants or to the environment in general, and/or the appearance of favourable new properties not inherent in the individual constituents.

The mixtures according to the invention render possible the sustained control of, in particular, the following principal weeds occurring in rice crops:

- Lindernia pyxidaria
 Limncharis flava
 Lobelia sp.
 Ludwigia angustifolia
 Ludwigia prostrata
 Ludwigia repens
 Marsilea crenata
 Marsilea minuta
 Melampodium sp.
 Monochoria vaginalis
 Nymphaea stellata
 Oenanthe javanica
 Paspalum dilatatum
 Paspalum distichum
 Paspalum esrobiculatum
 Polygonum spp.
 Polytrias amaura
 Portulaca oleracea
 Potamogeton spp.
 Rotala indica
 Sagittaria pygmaea
 Scirpus lateriflorus
 Scirpus maritimus
 Sphenoclear zeylanica
 Trianthema portulacastrum
 Vandellia sp.

concentrates, wettable powders, dusts, scattering powders, or granules.

The sprayable solutions for direct application contain, for example, mineral oil fractions having a high to medium boiling range, particularly a range above 100° C., for example diesel oil or kerosene, also coal tar oil or vegetable or animal oils, and also hydrocarbons, for example alkylated naphthalenes, tetrahydronaphthalene, xylene mixtures, cyclohexanols; and optionally too, moreover, ketones, chlorinated hydrocarbons, such as tetrachloroethane, trichloroethylene or tri- and tetrachlorobenzenes.

The aqueous application forms used are emulsion concentrates, pastes, or wettable

powders, with the addition of water. Suitable emulsifying agents or dispersants are non-ionic products, for example, condensation products of aliphatic alcohols, amines or carboxylic acids containing a long chain hydrocarbon radical of about 10 to 30 carbon atoms and ethylene oxide, for example the condensation product of octadecylalcohol and 25 to 30 moles of ethylene oxide, or that of soya fatty acid and 30 moles of ethylene oxide, or that of industrial oleylamine and 15 moles of ethylene oxide, or that of dodecylmercaptan and 12 moles of ethylene oxide. However, condensation products of ethylene oxide and hydroaromatic polycyclic carboxylic acids or amines may also be used. Among the anionic emulsifying agents that can be used there may be mentioned: the sodium salt of dodecylalcohol sulphuric acid ester, the sodium salt of dodecylbenzenesulphonic acid, the potassium or triethanolamine salt of oleic acid or abietic acid or of mixtures of these acids, or the sodium salt of a petroleumsulphonic acid. Suitable cationic dispersants are quaternary ammonium and phosphonium compounds such, for example, as cetylpyridinium chloride or dioxyethylbenzyl-dodecylammonium chloride.

If the agents according to the invention are used in the form of dusts or scattering agents, they may contain as solid carriers talcum, kaolin, bentonite, sand, calcium carbonate, calcium phosphate, also charcoal, cork powder, sawdust and other substances of vegetable origin.

It is possible to manufacture dusts having a content of 5—10% of the active mixture by diluting a wettable powder with a finely divided solid carrier. Wetting agents and dispersants can also be omitted or replaced by others. The various preparations can contain in conventional manner an admixture of substances that improve the distribution, fixation or penetrability. Examples of such substances are fatty acids, resins, glue, casein or alginates. The application of granules has proved very advantageous in combating weeds in rice, chiefly in water rice. Such granules are manufactured by dissolving the active substance mixture in an organic solvent and applying the resulting solution to a granulated mineral, for example attapulgit, SiO_2 , granicalcium, bentonite and the like, and then evaporating the solvent.

It is also possible to use polymer granules. They are prepared by mixing the active substances with polymerisable compounds (urea/formaldehydes, dicyandiamide/formaldehyde, melamine/formaldehyde or others), whereupon a mild polymerisation is carried out that does not affect the active substances, and the granulation is performed during the gel formation. It is more advantageous to impregnate finished porous polymer granules (urea/formaldehyde, polyacrylonitrile, polyester or others) which have a specific surface and favourable adsorp-

tion/desorption ratio with the active substances, for example in the form of their solutions (in a low boiling solvent) and to remove the solvent.

Polymer granules of this kind can be distributed in the form of microgranules having bulk densities of preferably 300 g/litre to 600 g/litre using atomisers. The dusting can be carried out from aircraft over extensive areas.

Additional fertilisers, surface-active agents or substances for increasing the specific weight, such as BaSO_4 , can of course be added to the granules.

It is also possible to obtain granules by compacting the carrier with the active substances and additives and then pulverising the product.

The concentration of active substance in herbicidal agents is preferably 0.1—95% by weight, most preferably 5 to 85% by weight.

Formulation Examples.

Wettable powder

The following components are mixed and finely ground to manufacture a wettable powder which is soluble in water:

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

Emulsion concentrate

- a) 40 Parts of an active substance mixture are mixed with 10 parts of a mixture of an anionic surface-active compound, preferably the calcium or magnesium salt of monolaurylbenzenemonosulphonic acid, and a non-ionic surface-active compound, preferably a polyethylene glycol ether of monosorbitol-laureate, and the whole is dissolved in xylene. The solution is made up with xylene to a volume of 100 ml to give a clear solution which can be used as spray concentrate and yields a stable emulsion by pouring it into water.

- b) Readily soluble active substances can also be formulated as emulsion concentrate according to the following prescription:

- 20 parts of active substance mixture
 - 70 parts of xylene and
 - 10 parts of a mixture of a reaction product of an alkylphenol and ethylene oxide and calcium-dodecylbenzene sulphonate
- are mixed. A sprayable emulsion is obtained by diluting the mixture with water in the desired concentration.

Granules

- a) 7.5 Grams of an active substance mixture are dissolved in 100 ml of acetone and the resulting acetonic solution is poured on 92 g

of granulated attapulgite (mesh size; 24/28 mesh/inch). The whole is well mixed and the solvent evaporated off in a rotary evaporator. Granules containing 7.5% of active substance are obtained.

b) To manufacture polymer granules containing 10% of active substance, 1050 to 1100 g of industrial active substance mixture are dissolved in 2 litres of trichloroethylene and the solution is sprayed in a fluidised bed granulator at 1.5 gauge pressure on to 9230 g of prepared urea/formaldehyde granules. The solvent can be removed by heating the air spirals to about 50° C.

c) To manufacture loaded granules containing 7.5% of active substance, 770 g. of a solid industrial active substance mixture, 500 g of BaSO₄, 1000 g of urea and 7730 g of powdered, porous polyacrylonitrile are moulded in a roll mill and the product subsequently broken up to the desired granular size.

Herbicidal Test

1. Test: 3—4 week old rice plants (height: 12—15 cm) reared in a rice field are transplanted in a test field covered with a layer of water to a depth of 3—5 cm.

a) Postemergent: After 8—12 days the field with its naturally sprouting weeds is treated once with the active substance or active substance mixture under test.

b) At emergent: After 4 days the field is treated once with the active substance or active substance mixture under test while the weeds are sprouting.

Evaluation takes place in such case 7—8 weeks after the treatment with the herbicide.

At various rates of application damage to the plants was effected as expressed by the percentages in tables 1 and 2. Herein:

IA=O,O - di - n - propyl - dithiophosphoryl - aceto - cyclohexamethylene imide,

IB=O,O - di - n - propyl - dithiophosphoryl - aceto - 2 - methylpiperidide,

IIA=2 - methylthio - 4 - ethylamino - 6- α,β - dimethylpropylamino) - s - triazine,

IIB=2 - methylthio - 4 - ethylamino - 6-tert.butylamino - s - triazine,

IIIA=2,4 - dichlorophenoxyacetic acid isopropyl ester.

It follows from the result that active substance (A5) mixtures according to the invention achieve not only an additively improved action against weeds, but that primarily at low concentrations they effect an almost total destruction of weeds that occur naturally in rice cultures, for example Echinochloa, Monochoria, Sagittaria, Eleocharis, Cyperus, Rotala, Lindernia, Vandellia and others. The slight damage caused to the rice culture observed at higher rates of application with pure s-triazine herbicides is, surprisingly, very largely eliminated when these latter are used in admixture with dithiophosphates of the formula I.

TABLE 1
Post-Emergence Application

Preparation	Rate of application in kg AS/ha	General action on weeds %	Special action on weeds (Monochoria) %	Special action on weeds (Sagittaria) %	Action on rice Damage in %
IA	1	20	60	40	0
	2	45	65	45	0
	4	50	70	50	0
	8	65	80	65	1,5
IB	1	35	75	40	0
	2	40	80	40	0
	4	40	85	45	0
	8	50	99	50	1
IIA	0.5	65	—	65	0
	1	80	85	70	4
	2	85	90	85	4
	4	—	96	—	4
IIB	0.5	75	—	65	2
	1	80	75	70	4
	2	90	80	90	15
	4	—	85	—	—
IA+IIA (4:1)	0.8+0.2	90	95	94	0
	1.6+0.4	96	96	98	1
	3.2+0.8	98	98	98	2
	6.4+1.6	99	100	99	4
IB+IIA (4:1)	0.8+0.2	90	95	90	0
	1.6+0.4	96	98	98	1
	3.2+0.8	98	99	99	2
	6.4+1.6	99	100	99	4
IB+IIB (4:1)	0.8+0.2	95	—	95	0
	1.6+0.4	97	—	99	0
	3.2+0.8	99	—	99.5	2
	6.4+1.6	100	—	100	3

TABLE 2
At emergence Application

		%	
IA	0,5 1,0	60 90	0 0
IB	0,5 1,0	75 90	0 0
IIIA	0,5 1,0	80 92	0 0
IA+IIIA	0,75+0,5 1,0 +0,5	99 100	0 0
IB+IIIA	0,75+0,5 1,0 +0,5	99,5 99,5	0 0

2. Test: For a special test on important weeds in rice crops, 3—4-week old rice plants grown in a rice field (height of plants 12—15 cm) are transplanted to an experimental field free from emerged weeds and with a water layer ca. 3—5 cm deep, the most important weeds appearing on this field being *Echinochloa crus galli* and *Eleocharis acicularis*.

The field, on which has occurred the natural emergence of weeds, is treated once, after 14 days, with the active substance or with the active-substance mixture (post-emergent). The mean outside temperature is 30° C.

An evaluation of the results is made 4 weeks after application.

Preparation	Applied amount of A.S. per hectare	Action against Echin. in %	Action against Eleoch. in %	Damage to rice plants in %
Ia	2.0	90	95	2
IIa	0.5	60	95	0
Ia+IIa (4:1)	1.6+0.4	95	100	0
Ib	2.0	95	98	0
Ib+IIa (4:1)	1.6+0.4	100	100	0

20 The action of the individual compounds with applied amounts of 2.0 and 0.5 kg of A.S./hect. respectively, against weeds is less than that of a 4:1-A.S.-mixture in which the proportion of individual components is only 1.6 and 0.4 kg of A.S./hectare, respectively.

25 3. Test: 3—4-Week old rice plants (height 12—15 cm) grown in a rice field were transplanted to a test field having a ca. 3—5 cm

deep water layer.

The field was treated after 4 days, before emergence of the naturally occurring weeds, with the active substance, or active substance mixture, in the form of a 7.5% granulate (pre-emergent application).

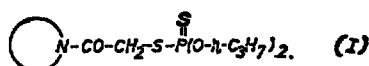
The results of the evaluation made after 6 weeks, and the crop yield after 17 weeks are given in the table below:

Preparation	Applied amount of A.S. per hectare	General action on weeds %	Damage to rice plants %	Rice yield in 1000 kg/hect.
Ib	1.0	95	0	3.1
IIIa	0.8	90	0	3.6
Ib+IIIa (1:1)	0.5+0.5	99	2	3.8

5 The action of the individual compounds with amounts of 1.0 and 0.8 kg of active substance per hectare, respectively, against weeds is less than that of a corresponding 1:1-active-substance mixture in which each proportion is only 0.5 kg of active substance per hectare. At the same time, an improvement in crop yield results from the application of 10 the active-substance mixture.

WHAT WE CLAIM IS:—

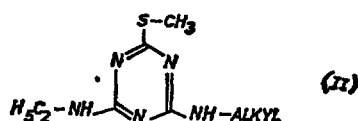
1. A synergistic herbicidal composition for the control of weeds in rice crops, which composition comprises
15 (A) a compound of the formula I



wherein the group

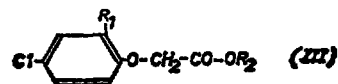


- 20 represents a cyclohexamethyleneimine radical or a 2-methylpiperidyl group and
(B) at least one compound of formula II:



wherein "alkyl" represents an alkyl group of 2 to 5 carbon atoms; or

- 25 (C) at least one growth hormone of formula III:



wherein R₁ represents a chlorine atom or a methyl group and R₂ represents a hydrogen atom, an alkali metal atom or an alkyl radical of 1 to 8 carbon atoms. 30

2. A composition according to claim 1 wherein the weight ratio of component A:B or A:C is 10:1 to 1:3.

3. A composition according to claim 2 35 wherein the weight ratio of component A:B or A:C is 6:1 to 1:1.

4. A composition according to any one of claims 1 to 3 wherein component B is 2-methylthio - 4 - ethylamino - 6 - α,β - di- 40 methylpropylamino) - s - triazine.

5. A composition according to any one of claims 1 to 3 wherein component B is 2-methylthio - 4 - ethylamino - 6 - t-butyl- 45 amino-s-triazine.

6. A composition according to any one of claims 1 to 3 wherein, in component C, R₂ represents an alkyl radical of 1 to 4 carbon atoms.

7. A composition according to claim 6 wherein component C is the isopropyl ester of 2,4-dichlorophenoxyacetic acid. 50

8. A composition according to claim 1 substantially as described in any one of the foregoing Formulation Examples. 55

9. A method of controlling weeds in rice crops which method comprises applying to a rice field a composition as claimed in any one of the preceding claims.

10. A method according to claim 9 substantially as hereinbefore described. 60

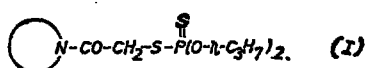
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Preparation	Applied amount of A.S. per hectare	General action on weeds %	Damage to rice plants %	Rice yield in 1000 kg/hect.
Ib	1.0	95	0	3.1
IIIa	0.8	90	0	3.6
Ib+IIIa (1:1)	0.5+0.5	99	2	3.8

- The action of the individual compounds with amounts of 1.0 and 0.8 kg of active substance per hectare, respectively, against weeds is less than that of a corresponding 1:1 active-substance mixture in which each proportion is only 0.5 kg of active substance per hectare. At the same time, an improvement in crop yield results from the application of the active-substance mixture.

WHAT WE CLAIM IS:—

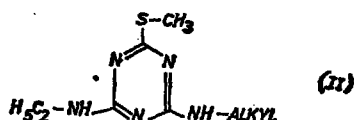
1. A synergistic herbicidal composition for the control of weeds in rice crops, which composition comprises
- 15 (A) a compound of the formula I



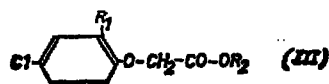
wherein the group



- 20 represents a cyclohexamethyleneimine radical or a 2-methylpiperidyl group and
- (B) at least one compound of formula II:



- wherein "alkyl" represents an alkyl group of 2 to 5 carbon atoms; or
- 25 (C) at least one growth hormone of formula III:



wherein R₁ represents a chlorine atom or a methyl group and R₂ represents a hydrogen atom, an alkali metal atom or an alkyl radical of 1 to 8 carbon atoms.

2. A composition according to claim 1 wherein the weight ratio of component A:B or A:C is 10:1 to 1:3.

3. A composition according to claim 2 wherein the weight ratio of component A:B or A:C is 6:1 to 1:1.

4. A composition according to any one of claims 1 to 3 wherein component B is 2-methylthio - 4 - ethylamino - 6 - α,β - dimethylpropylamino) - s - triazine.

5. A composition according to any one of claims 1 to 3 wherein component B is 2-methylthio - 4 - ethylamino - 6 - t-butylamino-s-triazine.

6. A composition according to any one of claims 1 to 3 wherein, in component C, R₂ represents an alkyl radical of 1 to 4 carbon atoms.

7. A composition according to claim 6 wherein component C is the isopropyl ester of 2,4-dichlorophenoxyacetic acid.

8. A composition according to claim 1 substantially as described in any one of the foregoing Formulation Examples.

9. A method of controlling weeds in rice crops which method comprises applying to a rice field a composition as claimed in any one of the preceding claims.

10. A method according to claim 9 substantially as hereinbefore described.

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