

PATENT SPECIFICATION

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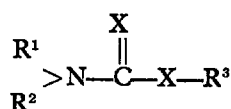


(54) HERBICIDAL COMPOSITIONS

(71) We, KUMIAI KAGAKU KOGYO KABUSHIKI KAISHA of No. 32, Sakuragaoka-Cho, Shibuya-Ku, Tokyo, Japan, a company organized according to the laws of Japan, 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 statements:—

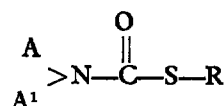
This invention relates to herbicidal compositions containing S-benzylthiocarbonates, and to a method of freeing rice fields from noxious weeds.

British Patent Specification number 886425 describes and claims herbicidal compositions, the active ingredients whereof are benzyl thiocarbonates of the general formula



wherein each X is an oxygen or sulphur atom, at least one being sulphur; R¹ and R² are selected from hydrogen atoms, alkyl, alkoxyalkyl, carboxyalkyl, carbamylalkyl, cycloalkyl, alkenyl, and haloalkenyl groups having up to seven carbon atoms or are linked together to form a group Cu Hzn in which n is an integer from 4 to 8 and which may be interrupted by an oxygen atom or by a group —NY— in which Y is a hydrogen atom or an alkyl or hydroxyalkyl group; and R³ is a benzyl, methylbenzyl or halogen substituted benzyl group containing not more than four nuclear halogen atoms; mono- and dialkylamino-S-benzylthio carbonates are not specifically exemplified.

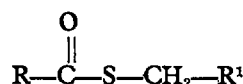
British Patent Specification number 995497 describes and claims herbicidal compositions, the active ingredients whereof are dialkylthiol-carbamates of the formula



wherein A and A¹ are selected from alkyl groups having from 2 to 4 carbon atoms and R is selected from benzyl, *m*-chlorobenzyl, 2,5-dichlorobenzyl, 2,6-dichlorobenzyl, 2,3,6-trichlorobenzyl, and 2-methoxy-5-chlorobenzyl groups.

The above-mentioned British Patent Specifications (hereinafter referred to as "the references") state that the active compounds disclosed therein have a contact killing activity, when applied to the foliage of plants and that they have a pre-emergence activity in an amount of $\frac{1}{4}$ to 100 pounds per acre and effect soil sterilization in an amount of 30 to 100 pounds per acre. The references also state that 3-chloro, 2,5-dichloro-, or trichloro benzyl N,N-diethyl-thio-carbamates described therein are considerably toxic to grass, bean and broad-leaved weed as contact herbicides, but they do not disclose the application of such herbicides to paddy rice fields, nor the selective activity of such herbicides when applied to rice fields.

Accordingly the present invention provides a selective herbicidal composition comprising as a major proportion a solid diluent or liquid diluent containing a surface active agent and as an active ingredient as S-benzylthio-carbamate of the general formula V:



V

wherein R is a mono- or dialkylamino group and R¹ is selected from 4-chlorophenyl, 2-chlorophenyl, methylphenyl, bromophenyl, 2,4-dichlorophenyl, 3,4-dichlorophenyl, di-

methylphenyl, methylchlorophenyl and methylbromophenyl groups.

Further, the present invention provides a method of manufacturing the herbicidal composition aforesaid, comprising associating a major proportion of an inert diluent with an active ingredient comprising an S-benzylthiocarbamate of the general formula V aforesaid.

Still further the present invention provides a method of freeing rice fields from undesirable plants, comprising applying to a rice field a herbicidally effective amount of the herbicidal composition aforesaid.

Our copending British Patent Application No. 18525/71 (Serial No 1259472) describes and claims *inter alia* a method of manufacturing the S-benzylthiocarbamates used as active ingredients in the herbicidal compositions of this invention, and also several of such S-benzylthiocarbamates which are novel compounds.

Herbicidal compositions applied previously to paddy fields have included PCP (pentachlorophenol), MO (active ingredient: 4-nitro-2',4',6'-trichlorodiphenyl ether), 2-methylthio-4,6-bis(ethylamino)-S-triazine and other numerous compositions, but most of these have been used for controlling germination of weeds after paddy rice plants have been planted. These previous herbicidal compositions are effective against therophyte weeds generated at a relatively early stage after planting of the rice plant, but have extremely poor and 0.048 times the entire focal length of the activity or substantially no activity for Wiregrass, a perennial weed. Recently, this Wiregrass has become a problem as the predominant weed in rice paddy, because any herbicidal composition, which has no phytotoxicity to paddy rice plant and can prevent growth only of Wiregrass, has never been discovered.

The reason why Wiregrass has grown in paddy is based on the fact that, in general, the previous herbicidal compositions are spread 3 to 7 days after the rice plant is planted, while generation of Wiregrass is about 2 weeks after planting; that is, Wiregrass is generated when the activity of the herbicidal

compositions is decreased, and, further, Wiregrass is perennial, so that it has a high resistance against the herbicidal composition.

The most active composition for preventing Wiregrass has been DBN (active ingredient: 2,6-dichlorobenzonitrile), but this composition is highly phytotoxic to paddy rice plants, so that it is dangerous to use in practice.

However, the herbicidal compositions according to the present invention have excellent activity for preventing Wiregrass, and particularly when they are used in the primary stage of growth of Wiregrass, the Wiregrass then completely being prevented even if an amount of less than 500 g/10 ares is applied. Particularly, when the surface layer of soil or water in a paddy field is supplied with an amount of from 100 to 250 g/10 ares before germination of the weed, the growth of weeds, such as Wiregrass, Barnyard grass and Crabgrass, can be prevented and paddy rice plants which are planted in a depth of more than 2 cm are not damaged. When 800 to 1,000 g/10 ares are used, the growth of the rice plants is slightly suppressed temporarily but thereafter, is not effected and the herbicidal compositions of the invention cause no damage.

Furthermore, when a S-benzylthiocarbamate in the herbicidal composition is supplemented with PCP (pentachlorophenol) or a salt thereof, a chlorophenoxy-herbicide, triazine-herbicide or a diphenylether-herbicide various weeds including the perennial weed Wiregrass can be prevented completely. When the S-benzylthiocarbamate is supplemented in this way, R¹ may optionally be methylphenyl. Also, a high herbicidal activity can be obtained when the supplemented herbicidal composition is used in an amount of only 1/10 to 1/5 the amount of either compound used alone, and an apparent synergistic effect can be recognised. The most effective weight ratio of S-benzylthiocarbamate to PCP in the supplemented herbicidal composition is from 1:0.5 to 1:10.

Typical S-benzylthiocarbamates that may be used in the present invention are:—

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|-----|---|------------------------------|
| (1) | S-(2-chlorobenzyl)-N-ethylthiocarbamate | B.P. 143—147°C/0.03mm Hg |
| (2) | S-(4-chlorobenzyl)-N,N-diethylthiocarbamate | B.P. 127—131°C/0.12mm Hg |
| (3) | S-(2-bromobenzyl)-N,N-diisopropylthiocarbamate | B.P. 152—156°C/0.04mm Hg |
| (4) | S-(2,4-dichlorobenzyl)-N,N-diisopropylthiocarbamate | B.P. 142—144°C/0.02mm Hg |
| (5) | S-(4-methylbenzyl)-N,N-diethylthiocarbamate | B.P. 107—115°C/0.002mm Hg |
| (6) | S-(2-methylbenzyl)-N,N-di-n-butylthiocarbamate | B.P. 108—112°C/0.00555 mm Hg |
| (7) | S-(3,4-dichlorobenzyl)-N,N-diethylthiocarbamate | B.P. 138—142°C/0.02mm Hg |
| (8) | S-(4-methylbenzyl)-N,N-diethylthiocarbamate | M.P. 35—37°C |
| (9) | S-(4-chlorobenzyl)-N,N-diisopropylthiocarbamate | B.P. 141—144°C/0.04mm Hg |
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The inert diluent used may be any carrier or surfactant usually used to prepare dust, emulsifiable concentrate and wettable powder types of herbicidal compositions, which are used directly or after dilution with water.

Furthermore, the herbicidal compositions of this invention may be prepared in the form of granular compositions. That is, the active ingredient may be mixed with bentonite, clay, talc, lime stone and/or other herbicide, and a binder, such as PVA (polyvinyl alcohol), and the resulting mixture kneaded with water and subjected to an extrusion type of granule forming machine; the formed granules are dried. Alternatively, the active ingredient may be dissolved in a solvent and the solution homogeneously adsorbed into, for example, granular diatomaceous earth or vermiculite.

Further alternatively, the surface of granular lime stone may be coated uniformly with the active ingredient. The granules thus obtained are dispersible uniformly, for example, by hand, granule spreader or helicopter.

The term "carrier" as used herein means any carrying agent, which may be solid or liquid, used for transferring the active in-

redient to desired areas. For example, as a solid carrier, clays, talc, kaolin, diatomaceous earth, calcium carbonate, hydrated silica or saw dust may be used. As a liquid carrier, use may be made of a solvent for the active ingredient or a liquid which is non-solvent but which can disperse or dissolve the active ingredient by means of the presence of an adjuvant, for example, water, benzene, kerosene, alcohol, acetone, methylnaphthalene or xylene.

The term "surfactant" used herein and in the claims means a non-ionic surfactant, such as polyoxyethylenealkylaryl ether or polyoxyethylenesorbitane monolaurate; a cationic surfactant, such as alkyltrimethylbenzyl ammonium chloride or alkylpyridinium halide; an anionic surfactant, such as an alkylbenzene sulfonate or fatty alcohol sulfate; or an amphoteric surfactant, such as a lauryl amine derivative; a betaine derivatives or dodecyl diaminoethyl glycine.

The invention will be further explained in detail with reference to the following preparative examples:

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EXAMPLE 1 Wettable powder

Twenty five parts by weight of S-(2-chlorobenzyl)-N-methylthiocarbamate, 10 parts by weight of hydrated silicon dioxide, 60 parts by weight of diatomaceous earth and 5 parts by weight of wetting agent comprising a mixture of polyoxyethylenealkyl phenol ether, polyoxyethylenephenylphenol ether and polyoxyethylene carbonate were mixed and milled and the resulting powder was suspended in water, which was sprayed.

EXAMPLE 2 Granule

Five parts by weight of S-(4-chlorobenzyl)-N,N-diethylthiocarbamate were sprayed on and adsorbed in 95 parts by weight of granular diatomaceous earth, with stirring; the diatomaceous earth had a particle size ranging from 10 to 100 mesh Japanese Industrial Standards (1.68 mm to 0.149 mm).

EXAMPLE 3 Emulsifiable concentrate

Fifty parts by weight of S-(4-chlorobenzyl)-N,N-diethylthiocarbamate, 30 parts by weight of xylene and 20 parts by weight of an emulsifier comprising a mixture of polyoxyethylenealkylphenol ether, polyoxyethylenephenylphenol ether and polyoxyethylene carbonate were mixed and dissolved. The resulting solution was diluted with water and then sprayed.

EXAMPLE 4 Granule

Five parts by weight of S-(4-chlorobenzyl)-N,N-diethylthiocarbamate, 15 parts by weight of PCP (pentachlorophenol) sodium salt, 50 parts by weight of bentonite, 27 parts by weight of clay, 1 part by weight of sodium alkylarylsulfonate and 2 parts by weight of sodium ligninsulfonate were mixed and milled and then added with a suitable amount of water and kneaded; the kneaded mixture was subjected to extrusion in a type of granule forming machine having an opening of 1 mm diameter to obtain granules, which were dried.

EXAMPLE 5 Granule

Seven parts by weight of S-(4-chlorobenzyl)-N,N-diethylthiocarbamate, 10 parts by weight of PCP sodium salt, 10 parts by weight of diatomaceous earth, 40 part by weight of bentonite, 30 parts by weight of clay, 2 parts by weight of sodium alkylsulfonate and 10 parts by weight of PVA were mixed and milled and added to a suitable amount of water. The resulting mixture was kneaded and then subjected to extrusion in a type of granule forming machine having an opening of 1 mm diameter to form granules which were dried.

EXAMPLE 6 Wettable powder

12.5 parts by weight of S-(4-chlorobenzyl)-N,N-diethylthiocarbamate, 25 parts by weight of PCP, 30 parts by weight of clay, 29.5 parts by weight of diatomaceous earth, 1 part by weight of polyoxyethylenealkylaryl ether and 2 parts by weight of sodium ligninsulfonate were mixed and milled to obtain a wettable powder.

In order to show the activity of the herbicidal compositions of the present invention, the following experimental examples are given.

EXPERIMENTAL EXAMPLE 1

Three groups of 3-leaf stage young paddy rice plant (species: KINMAZE), one group of which has two rice plants, were planted in pots of 15 cm diameter. After the rice plant had taken, 30 Barnyard grass seeds per pot were sowed on the surface layer of the soil and the pots were filled with water to a depth of 1 cm. One day later granular compositions containing 5% by weight active ingredients of the present invention (Example 2) were spread in such amounts that the amounts of active ingredients were 100 g, 250 g and 500 g per 10 ares. Two weeks after the treatment, the growth degree of the weed and the phytotoxicity on the paddy rice plants were estimated.

Active Ingredient	Dose g/10a	Number of Barnyard grass plants	Number of broad leaf weeds	Phytotoxicity on paddy rice plant
Compound 1	500	0	0	No damage
"	250	1	2	"
"	100	5	11	"
Compound 2	500	0	0	"
"	250	0	1	"
"	100	2	1	"

Active Ingredient	Dose g/10a	Number of Barnyard grass plants	Number of broad leaf weeds	Phytotoxicity on paddy rice plant
Compound 3	500	0	0	No damage
„	250	0	3	„
„	100	1	5	„
Compound 4	500	0	0	„
„	250	0	2	„
„	100	2	9	„
Compound 5	500	0	0	„
„	250	0	0	„
„	100	1	1	„
Compound 6	500	0	0	„
„	250	2	4	„
„	100	5	12	„
Compound 7	500	0	0	„
„	250	0	1	„
„	100	1	2	„
Compound 8	500	0	0	„
„	250	1	2	„
„	100	2	7	„
Compound 9	500	0	0	„
„	250	1	1	„
„	100	1	3	„
Comparative compounds				
Compound 10	500	1	4	Heavy damage
„	250	4	8	Slight damage
„	100	7	13	No damage
Compound 11	500	1	5	Heavy damage
„	250	5	12	Slight damage
„	100	7	16	No damage
Compound 12	500	0	2	Heavy damage

Active Ingredient	Dose g/10a	Number of Barnyard grass plants	Number of broad leaf weeds	Phytotoxicity on paddy rice plant
Compound 12	250	3	6	Slight Damage
„	100	6	12	No damage
Compound 13	500	1	4	Heavy damage
„	250	5	9	Slight damage
„	100	7	15	No damage
Non-treated	0	28	33	„

- Compound 10 comprises as an active ingredient S - benzyl - N,N - diethylthiocarbamate,
- 5 compound 11 comprises S - (2,3,6 - trichlorobenzyl) - N,N - diethylthiocarbamate, compound 12 comprises S - (4 - chlorobenzyl) - N,N-diethyldithiocarbamate and
- 10 compound 13 comprises S - (2,6 - dichlorobenzyl) - N,N-diethyldithiocarbamate.

EXPERIMENTAL EXAMPLE 2

Pots of 12 cm diameter were filled with upland soil, wheat and radish seeds were sowed in

the pots and then the pots were covered with soil in a depth of 2 cm. In this case, the covering soil had been previously mixed with Crabgrass seeds. One day after covering the pots with soil, there were applied the suspensions obtained by diluting the wettable powders having 50% by weight of the active ingredients with 10 ml of water. The amounts applied were as shown in the following table; The suspensions were sprayed uniformly on the soil surface. The determination was made three weeks after the spraying.

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Active ingredient	Dose g/10a	Crabgrass* (g)	Wheat	Radish
Compound 1	500	0.2	±	±
„	250	3.2	—	—
„	100	6.7	—	—
Compound 2	500	0	±	±
„	250	1.3	—	—
„	100	7.3	—	—
Compound 3	500	0.1	+	±
„	250	4.2	—	—
„	100	9.0	—	—
Compound 4	500	0	+	±
„	250	2.8	—	—
„	100	8.3	—	—
Compound 5	500	1.3	±	+
„	250	2.8	—	—
„	100	6.0	—	—
Compound 6	500	0.8	+	±
„	250	1.6	—	—
„	100	5.8	—	—
Non-treated	0	10.8	—	—

Note: —: no damage

±: very slight damage

+: slight damage

*: weight of living plant 3 weeks after treatment.

EXPERIMENTAL EXAMPLE 3

5 Pots of 15 cm diameter were fed with paddy soil containing Wiregrass root and then filled with water. Two days after the filling, there were applied the suspensions obtained by diluting the wettable powders having 25% by weight of the active ingredients with 5 ml of water; the amounts applied are shown in the

following Table. The suspensions were 10
dropped on the pot and the thus treated pots
were left to stand in a green-house. Two
weeks after the treatment, the growth state of
Wiregrass was estimated and a further one 15
month later the weight of the living plants of
Wiregrass was determined. The results ob-
tained are as follows:

Active ingredient	Dose g/10a	State two weeks after treatment	Weight of living plant one month after treatment (g)
Compound 1	100	++	0.8
„	250	+	0.01
„	500	—	0
Compound 2	100	—	0.01
„	250	—	0
„	500	—	0
Compound 3	100	+	1.0
„	250	—	0.1
„	500	—	0
Compound 4	100	+	1.3
„	250	±	0.3
„	500	—	0
Compound 5	100	+	0.7
„	250	±	0.3
„	500	—	0.1
Compound 6	100	++	1.2
„	250	±	0.3
„	500	—	0
Non-treated	0	+++	4.2

Note: —: no growth

±: slight growth

+: moderate growth

++: heavy growth

+++ : very heavy growth

EXPERIMENTAL EXAMPLE 4

5 Pots of 15 cm diameter were fed with paddy soil and planted with three groups of young paddy rice plants (species: KINMAZE), one group of which has two rice plants. After the rice plants had taken, 30 Barnyard grass seeds were sowed in the pots and then the herbicidal compositions of the invention (wetable

powder) and comparative compositions diluted 10 with water of 7 ml per pot as shown in the following Table were dropped on the pots. Three weeks after the treatment, the number of the generation of Barnyard grass, the number of broad leaf weeds naturally generated and the 15 phytotoxicity on paddy rice plant were determined.

Active ingredient	Dose per 10 ares (g)		Number of Barnyard grass	Number of broad leaf plant	Phyto-toxicity on paddy rice plant
Herbicide of this invention (Ex. 1)	S-(4-chloro-benzyl)-N,N-diethylthiocarbamate: sodium salt of PCP				
	500	—	13	23	±
„	250	—	21	34	—
„	100	—	29	33	—
Herbicide of this invention (Ex. 6)	250	+500	0	0	—
„	125	+250	0	0	—
„	50	+100	0	3	—
„	25	+50	3	7	—
Comparative composition * (PCP granule)	—	1,000	0	0	+
„	—	750	6	4	±
„	—	500	17	11	—
„	—	250	27	31	—
Non-treated	—	—	28	36	—

Note:

phytotoxicity on paddy rice plant: — : no damage,

± : very slight damage, + : slight damage

*: commercially available composition containing PCP sodium salt hydrate.

EXPERIMENTAL EXAMPLE 5

Plants to be tested: Wiregrass, Barnyard grass, paddy rice plant (KINMAZE)

5 Sizes of pot: Diameter: 15 cm

Compositions to be tested:

(1) Herbicidal composition of the invention

(Example 4)

(2) „ (Example 5)

10 (3) „ (Example 2)

(4) Granular composition of 25% sodium salt of PCP (commercially available)

Treatment:

(1) Soil containing Wiregrass roots was fed

into pots, three groups of young paddy rice plants (one group having two rice plants) were planted in the pots and then 20 Barnyard grass seeds were sowed in the pots. 24 hours later the pots were treated with the herbicidal compositions (treatment before germination)

(2) Wiregrass was planted in pots, the soil was covered with water and then the pots were treated with herbicidal compositions (treatment in growing stage).

The determination was made three weeks after the treatment.

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Active ingredient	Dose per 10 ares (Kg)	Amount of active ingredients per 10 ares		Wiregrass treatment before germination	Wiregrass treatment in the growing stage	Number of Barnyard grass	Phytotoxicity of paddy rice plant
		Sodium salt of PCP (g)	carbamate (g)				
Herbicide according to this invention (Example 4)	1	150	50	* 1 ** (0.7)	* 3 ** (3.1)	4	—
"	2	300	100	0 (0)	0 (0)	0	—
"	3	450	150	0 (0)	0 (0)	0	—
Herbicide according to this invention (Example 5)	1	250	70	0.5 (0.3)	2 (2.8)	2	—
"	2	200	140	0 (0)	1 (1.7)	0	—
"	3	300	210	0 (0)	0 (0)	0	—
Herbicide according to this invention (Example 2)	2	—	100	4 (3.0)	5 (5.3)	17	—
"	5	—	250	1.5 (1.1)	3 (4.0)	11	—
"	10	—	500	0 (0)	0 (0)	5	—
Sodium salt of PCP	1	250	—	5 (3.5)	5 (5.8)	19	—
"	2	500	—	5 (3.2)	5 (5.7)	7	—
"	3	750	—	4.5 (2.8)	5 (5.7)	1	+
Non-treated	0	—	—	5 (3.7)	5 (5.6)	18	—

Note:

*: growth degree of Wiregrass

**: weight of living plant of Wiregrass (g)

0: no growth

5: 100% growth

EXPERIMENTAL EXAMPLE 6

Test place: Paddy field (Alluvial loamy soil)

Test plant: Paddy rice plant (species: NORIN 29)

5 Planted date: June 18

Test area: 1 zone: 2.5m²

Treated date: June 23

Treatment: The composition to be tested was spread uniformly by hand when the paddy field was filled with water to a depth of 3 cm.

Sample:

(1) The herbicidal composition of the present invention (Example 4)

(2) PCP granular composition 25 (commercially available, granular composition of 25% PCP)

(3) Commercially available granular composition of 2.5% DBN (dichlorobenzonitrile).

Determined date: July 14 (weeds within 1 m²)

Active ingredient sample	Dose per 10 ares (Kg)	Grass weed		Broad leaf weed		Weight of living plant of Spikerush weight	Phytotoxicity on paddy rice plant
		Number	Weight (g)	Number	Weight (g)		
(1) Herbicide according to this invention (Example 4)	2	14	7.0	43	62	0.2	—
"	3	6	3.1	4	7.3	0	—
(2) PCP granule	2	41	98.3	107	186.0	5.4	—
"	3	7	6.2	41	72.0	8.6	+
(3) DBN granule	2	63	113.0	161	186.0	1.7	++
"	3	16	21.4	98	81.3	0	++
(4) Non-treated	0	94	216.0	208	321.0	9.7	—

Phytotoxicity on rice plant — : no damage

± : very slight damage

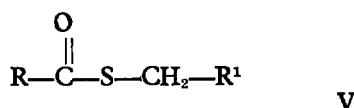
++ : moderate damage

+ : slight damage



WHAT WE CLAIM IS:—

- (1) A selective herbicidal composition comprising as a major proportion a solid diluent or liquid diluent containing a surface active agent and as an active ingredient an S-benzylthiocarbamate of the general formula V:



wherein R is a mono- or dialkylamino group and R¹ is selected from 4-chlorophenyl, 2-chlorophenyl, bromophenyl, 2,4-dichlorophenyl, 3,4-dichlorophenyl, dimethylphenyl, methylchlorophenyl and methylbromophenyl groups.

- (2) A herbicidal composition according to claim 1, wherein the active ingredient is supplemented with a herbicidal agent selected from pentachlorophenol, salts thereof, chlorophenoxy herbicides, triazine herbicides and diphenylether herbicides, and R¹ is optionally a methylphenyl group.

- (3) a herbicidal composition according to claim 2, wherein the herbicidal agent is pentachlorophenol or a salt thereof, and the weight ratio of S-benzylthiocarbamate to pentachlorophenol or salt thereof is within the range from 1:0.5 to 1:10.

- (4) A herbicidal composition according to any one of claims 1 to 3, wherein the inert diluent includes a solid material selected from bentonite, clay, talc and limestone, and a binder.

- (5) A herbicidal composition according to claim 4, wherein the binder is polyvinyl alcohol.

- (6) A herbicidal composition as claimed in any one of claims 1 to 3, wherein the active ingredient is in solution in a solvent therefor and the solution has been absorbed into a granular absorbent.

- (7) A herbicidal composition according to claim 6, wherein the granular absorbent is diatomaceous earth or vermiculite.

- (8) A herbicidal composition according to any one of claims 1 to 3, wherein the active ingredient is coated on granular limestone.

- (9) A herbicidal composition according to any one of claims 1 to 3, wherein the inert diluent includes a liquid.

- (10) A herbicidal composition according to claim 9, wherein the liquid is a solvent for the active ingredient.

- (11) A herbicidal composition according to claim 9, wherein the liquid is a non-solvent for the active ingredient and includes an adjuvant capable of dissolving or dispersing the active ingredient.

- (12) A herbicidal composition according to any one of claims 9 to 11, wherein the liquid is selected from water, benzene, toluene, kerosene, alcohol, acetone, methylnaphthalene

and xylene.

- (13) A herbicidal composition according to any one of claims 1 to 12, including a surfactant.

- (14) A herbicidal composition according to claim 13, wherein the surfactant is selected from polyoxyethylenealkylaryl ethers, polyoxyethylenesorbitane monolaurate, alkyl dimethylbenzylammonium chlorides, alkylpyridinium halides, alkylbenzene sulphonates, fatty alcohol sulphates, lauryl amine derivatives, and dodecyl diamono ethyl glycine.

- (15) A herbicidal composition according to claim 1 and substantially as herein before described.

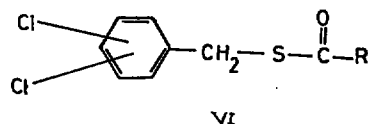
- (16) A herbicidal composition according to any one of Examples 1 to 6.

- (17) A method of manufacturing the herbicidal composition claimed in any one of claims 1 to 15, comprising associating a major proportion of an inert diluent with an active ingredient comprising an S-benzylthiocarbamate of the general formula given in claim 1.

- (18) A method of manufacturing a herbicidal composition according to any one of Examples 1 to 6.

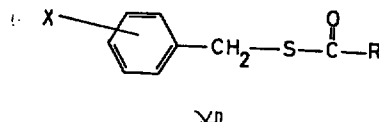
- (19) A method of freeing rice fields from undesirable plants, comprising applying to a rice field a herbicidally effective amount of the herbicidal composition claimed in any one of claims 1 to 16.

- (20) A method according to claim 19, wherein the herbicidal composition includes as active ingredient a thiocarbamate of the general formula VI.



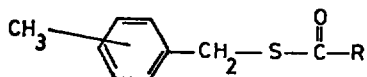
wherein R is as defined in claim 1 and the chlorine atoms occupy the 2- and 4- positions or the 3- and 4-positions of the phenyl ring.

- (21) A method according to claim 19, wherein the herbicidal composition includes as active ingredient a thiocarbamate of the general formula VII



wherein R is as defined in claim 1 and X is a chlorine atom occupying the 2- or 4- position of the phenyl ring, or is bromine.

- (22) A method according to claim 19, wherein the herbicidal composition includes as active ingredient a thiocarbamate of the general formula VIII



whereas R is defined in claim 1.

(23) A method as claimed in claim 21,
5 wherein the active ingredient is S-(4-chloro-
benzyl)-N, N-diethylthio-carbamate

(24) A method as claimed in claim 23,
wherein the active ingredient is supplemented
with another herbicide.

10 (25) A method as claimed in any one of
claims 19 to 24, wherein the undesirable plants

include Wiregrass.

(26) A method of freeing paddy rice fields
from undesirable plants, according to claim 19,
and substantially as hereinbefore described.

(27) A method of freeing rice fields from
undesirable plants, according to claim 19 and
substantially as herein before described with
reference to any one of Experimental Examples
1 to 6. 15

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