PATENT SPECIFICATION (11) 1 524 596

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(21) Application No. 36674/76 (22) Filed 3 Sept. 1976
(31) Convention Application No. 11458/75
(32) Filed 4 Sept. 1975 in
(33) Switzerland (CH)
(44) Complete Specification published 13 Sept. 1978
(51) INT CL² C07C 83/00; A01N 17/00
(52) Index at acceptance
C2C 220 226 227 22Y 30Y 326 346 376 63Y 656 791 79Y MD
A5E 1A2P 1A3B 1A3C 1A5B3 1C15A1 1C15A5 1C15A8 1C15B3 1C5M 1C8A

(19)

(54) NOVEL OXIME ETHER, PROCESSES FOR PREPARING IT, AND ITS USE AS ANTIDOTE FOR HERBICIDES WHICH DAMAGE CULTIVATED PLANTS OR IN SEED GERMINATION PROMOTION

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate, of 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 a novel oxime ether, its preparation, compositions containing it and its use. The oxime ether according to the invention may be used as an antidote (safener) for herbicides which damage cultivated plants, so that such herbicides can be employed, without substantial loss of their herbicidal action against weeds, in crops of cultivated plants. The oxime ether of the present invention may also be used in the promotion of the germination of seeds of cultivated plants.

It is known that many herbicides, such as triazines, urea derivatives, carbamates, thiolcarbamates, haloacetanilides, halophenoxyacetic acids, etc., may have in the case of cultivated plants an action that is not selective or insufficiently selective, with the result that the herbicides attack not only the weeds to be combated but to a lesser or greater extent also the cultivated plants.

Various substances have already been suggested for overcoming this problem, which substances are able to specifically antagonise the harmful action of the herbicide on the cultivated plant, i.e. to protect the cultivated plant without noticeably affecting the herbicidal action on the weeds to be combated. Depending on its properties, the antidote can be used before emergence (pre-emergence) or after emergence (post-emergence) of the plants: it can be used for pretreatment of the seed of the cultivated plant (seed dressing); or it can be applied into the seed furrows before sowing; or it can be used for the pretreatment of cuttings; or finally it can be applied as a tank mixture; whereby it can be employed on its own or together with the herbicide, and can be applied either by one or by several of these methods. The treatment with the antidote can be carried out before or after the herbicidal treatment, or the two treatments can be performed simultaneously. The pre-emergence treatment includes both the treatment of the cultivated area before sowing (ppi=pre plant incorporation) and the treatment of the sown cultivated area before emergence of the plants.

The suggested antidotes frequently have an action that is very "specific to the species" with regard to the cultivated plants (e.g. maize, cereals such as wheat, etc., rice, sorghum, soybean, cotton, sugar cane, etc.) and with regard to the type of active substance of the herbicide (triazines, carbamates, etc.) and often also with regard to the type of application (seed dressing, pre-emergence tank application, etc.), i.e. a specific antidote is frequently suitable only for a specific cultivated plant and for certain herbicidal classes of active substance.

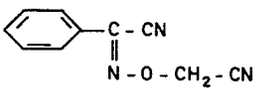
Thus British Patent Specification No. 1,277,557 describes the protective treatment of seed and of shoots of wheat and sorghum with certain oxamic acid esters and amides in order to avoid the harm caused by "Alachlor" (N - methoxymethyl - (2',6' - diethyl - chloroacetanilide). According to other references [German Offenlegungsschrift (DOS), Nos. 1,952,910 and 2,245,471, and French Patent Specification No. 2,021,611], antidotes are suggested for the treatment of cereals, maize seed and rice seed for protection against the attack from herbicidal thiolcarbamates. In German Patent Specification No. 1,576,676

and United States Patent Specification No. 3,131,509, there are suggested hydroxy-amino-acetanilides and hydantoins for the protection of the seed of cereals against carbamates such as IPC, CIPC, etc.

The direct treatment of certain useful plants before or after emergence of the plants on a cultivated area with antidotes as antagonists of specific classes of herbicides is described in German Offenlegungsschrift (DOS) Nos. 2,141,586 and 2,218,097 and in United States Patent Specification No. 3,867,444.

Whilst maize plants can be excellently protected from damage that can result from strongly herbicidally effective chloroacetanilides, such as have been described in German Offenlegungsschrift (DOS) Nos. 2,212,268, 2,305,495 and 2,328,340, by an N-substituted dichloroacetamide being applied as antidote to the soil (German Offenlegungsschrift No. 2,402,983), corresponding tests in other crops, such as cultivated millet and rice, have been unsuccessful.

It has now been found that surprisingly the novel oxime ether of formula I

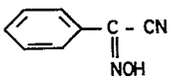


(I)

which can be designated as [O-(cyanomethyl)-oximino]benzylcyanide or as [O-(cyanomethyl) - oximino] - α - cyanotoluene or as phenylglyoxylonitrile - 2 - oxime - cyanomethyl ether, is excellently suitable for the protection of cultivated plants, such as maize, varieties of cereals (e.g. wheat, rye, barley, oats), cotton, sugar beet, sugar cane, soybean, especially however cultivated millet of the *Sorghum genus,* such as *S. vulgare* and *S. hybridum,* as well as rice, from the attack of herbicides such as triazines, phenylureas, carbamates, benzoic acid derivatives, halophenoxyacetic acids, particularly however from the attack of herbicidal haloacetanilides and thiocarbamates. Further the oxime ester may be used to promote germination of seeds of cultivated plants.

The free phenylglyoxylonitrile-2-oxime from which the above ether derives and some ring-substituted derivatives of the free oxime are described in United States Patent Specification No. 3,799,757 as growth inhibitors for regulating the growth in height of maize, cereals and soybean, i.e. for a completely different field of application.

The novel oxime ether of formula I may be prepared according to the invention by reaction of a salt, especially of an alkali metal salt, of phenylglyoxynitrile-2-oxime of formula II



(II)

with a cyanomethyl halide (haloacetonitrile) of the formula Hal—CH_2—CN.

The starting oxime of formula II is known and can be produced, for example, according to "Organic Reactions" (1953), Vol. 7, pp. 343 and 373. It is known that oximes can exist in two stereoisomeric forms, the syn- and anti-form. Also the oxime ether of formula I according to the invention can exist in both forms and as a mixture thereof. It is to be understood that the present invention includes both stereoisomeric forms either separately or as a mixture in any ratio.

The following Example illustrates the preparation of the novel oxime ether of formula I.

Example.

33.8 g of phenylglyoxylonitrile-2-oxime (sodium salt) is suspended in 200 ml of acetonitrile in a 350 ml sulphonating flask. An addition is then made dropwise of 15.1 g of chloroacetonitrile in 20 ml of acetonitrile, whereupon a very slight increase in temperature can be observed. The suspension is subsequently refluxed with stirring for 3 hours, during the process of which the reaction mixture assumes a light-green colour. After cooling to room temperature, the formed sodium chloride is filtered off with suction, and the filtrate is concentrated in a rotary evaporator to obtain as residue 31 g of crude product. This is dissolved in 200 ml of acetonitrile; the solution is stirred with charcoal and filtered until clear. Concentration of the filtrate in the rotary evaporator yields 25.4 g of oxime ether (68.6% of theory), m.p. 53—54° C.

Recrystallised from isopropanol, the pure phenylglyoxylonitrile - 2 - oxime - cyanomethyl ether melts at 56—47° C (syn-form). The other stereoisomeric form (anti) of this ether melts at 58—59° C and has a boiling point of 136° C/0.05 torr.

The invention provides a composition for combating weeds in a crop of cultivated plants, which composition contains at least one herbicide as herbicidally effective ingredient together with the oxime ether of the formula I as crop plant-protecting antidote.

The invention further provides a solid composition for use as a herbicide antidote which composition comprises, as active ingredient, the oxime ether of the formula I together with a solid extender and, optionally, a surface active agent, and a liquid composition which comprises the oxime ether together with a liquid diluent and a surface active agent.

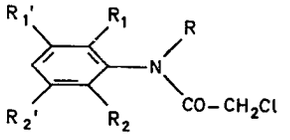
The oxime ether of the formula I may be used to combat selectively weeds in a crop

of cultivated plants by applying to a locus intended for sowing or already sown, or a locus on which the sown plants have already emerged simultaneously or successively in either order (i) a herbicide, and (ii) the oxime ether in an amount sufficient to protect the emerging or emerged cultivated plants from attack by the herbicide. Suitably the ground intended for sowing and provided with seed furrows is treated with a concentrated solid or liquid composition containing the oxime ether and the herbicide is applied after the seed furrows have been covered, before emergence of the plants.

Alternatively seeds of the cultivated plants may be dressed with the oxime ether of the formula I before sowing and the herbicide applied to the locus in which the seeds have been sown and before or after germination such as the emerging or emerged cultivated plants are protected from attack by the herbicide. Suitably the seed is dressed by shaking with a concentrated pulverent or liquid composition of the oxime ether to give uniform distribution of the oxime ether over the surface of the seed, the amount of the composition being such that 10 to 500 g of phenylglyoxylonitrile - 2 - oxime - cyanomethyl ether per 100 g of seed is used. The seed may also be dressed with an insecticidal, acaricidal and/or fungicidal and/or nematocidal substance.

Chloroacetanilide herbicides usable as highly effective active substances which on their own damage cultivated plants, such as cereals, maize, rice and cultivated millet varieties, but which when used together with the oxime ether according to the invention no longer appreciably attack these cultivated plants whilst retaining the herbicidal effectiveness against weeds, are described in, for example, German Offenlegungsschrift (DOS) Nos. 2,212,268, 2,305,495, 2,328,340, 2,402,983, 2,405,183 and 2,405,479.

The antidote according to the invention is preferably used together with herbicidal chloroacetanilides of the formula



wherein

each of R_1, R_1', R_2 and R_2', which may be the same or different, represents a hydrogen or halogen atom, or an alkyl, haloalkyl or alkoxy group having 1 to 4 carbon atoms, or an alkoxyalkyl or alkylthioalkyl group having 1 to 4 carbon atoms in each alkyl moiety, and

R represents an alkyl group having 1 to 4 carbon atoms which is substituted by one or more carboxy, carboxylic acid ester, carboxylic acid amide or cyano groups, or an alkoxyalkyl group of formula —A—O—R_3 (wherein A represents an alkylene group having 1 to 4 carbon atoms of which 1 or 2 are in the direct chain, and R_3 represents an alkyl or alkenyl group having up to 4 carbon atoms or a cycloalkyl or cycloalkylmethyl group having 3 to 6 ring carbon atoms).

Herbicidal chloroacetanilides preferably used are those where in the above formula

R_1 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms,

R_2 represent an alkyl group having 1 to 4 carbon atoms,

one of R_1' and R_2' represents a hydrogen atom and the other represents a hydrogen atom or an alkyl or alkoxy group having 1 to 4 carbon atoms, and

R represents an alkyl group having 1 to 4 carbon atoms which is substituted by one or more carboxylic acid ester groups, or an alkoxyalkyl group of the formula —A—O—R_3 (wherein A represents an alkylene group having 2 or 3 carbon atoms of which 1 or 2 are in the direct chain, and R_3 represents an alkyl or alkenyl group having up to 4 carbon atoms).

Some herbicidal chloroacetanilides which can be used are listed below:

N - 2' - methoxyethyl) - 2,6 - dimethyl-chloroacetanilide,

N - (2' - allyloxyethyl) - 2,6 - dimethyl-chloroacetanilide,

N - (2' - n - propyloxyethyl) - 2,6 - dimethyl-chloroacetanilide,

N - (2' - isopropyloxyethyl) - 2,6 - dimethyl-chloroacetanilide,

N - (2' - methoxyethyl) - 2 - methyl - 6-ethyl-chloroacetanilide,

N - (2' - methoxyethyl) - 2,6 - diethyl-chloroacetanilide,

N - (2' - ethoxyethyl) - 2 - methyl - 6-ethyl-chloroacetanilide,

N - (1' - ethoxycarbonyl - ethyl) - 2,6 - dimethyl-chloroacetanilide,

N - (3' - methoxy - propyl - (2') - 2-methyl-chloroacetanilide,

N - (3' - methoxy - propyl - (2') - 2,6-dimethyl-chloroacetanilide,

N - (3' - methoxy - propyl - (2') - 2-methyl-6-ethyl-chloroacetanilide,

N - (3' - methoxy - propyl - (2') - 2,6-diethyl-chloroacetanilide,

N - (3' - methoxy - propyl - (2') - 2-ethyl-chloroacetanilide,

N - (2' - ethoxyethyl) - 2,6 - diethyl-chloroacetanilide,

N - (2' - n - propoxyethyl) - 2 - methyl-6-ethyl-chloroacetanilide,

N - (2' - n - propoxyethyl) - 2,6 - diethyl-chloroacetanilide,

N - (2′ - isopropyloxyethyl) - 2 - methyl-6-ethyl-chloroacetanilide,

N - chloroacetyl - 2,6 - dimethylanilino-acetic acid ethyl and

N - chloroacetyl - 2,6 - dimethylanilino-acetic acid methyl ester,

β - (N - chloroacetyl - 2,6 - dimethyl-anilino)-propoinic acid methyl ester,

α - (N - chloroacetyl - 2 - methyl - 6-ethyl-anilino)-propionic acid ethyl ester,

N - (3′ - methoxy - propyl - (2′) - 2,3-dimethyl-chloroacetanilide,

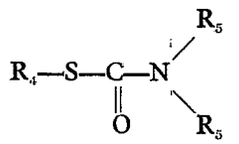
N - (2′ - ethoxyethyl) - 2 - methyl - 6-chloroacetanilide,

N - (2′ - methoxyethyl) - 2 - methyl - 6-chloroacetanilide,

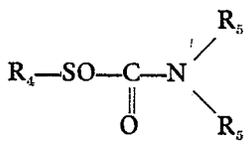
N - (2′ - methoxyethyl) - 2 - methyl - 6-methoxychloroacetanilide.

The herbicidal chloroacetanilides mentioned above and other herbicidal chloroacetanilides of this type and the production thereof have been described in the aforementioned German 'Offenlegungsschriften.'

Suitable thiolcarbamates which can be used as herbicides, especially in the case of pre-treatment of the seed with the novel oxime ether, are those of the general type:



or



wherein R_4 represents an alkyl group having 1 to 4 carbon atoms, and the R_5 groups are the same and represent alkyl groups having 3 or 4 carbon atoms;

the following may for example be mentioned:

S-ethyl-N,N-dipropylthiocarbamate and

S-ethyl-N,N-diisobutylthiocarbamate.

Further examples of utilisable herbicidal thiolcarbamates are disclosed by the United States Specifications Nos. 2,913,327, 3,037,853, 3,175,897, 3,185,720, 3,198,786 and 3,582,314.

The amount of the antidote used generally varies between about 0.01 and about 15 parts by weight per part by weight of haloacetanilide or thiolcarbamate. The most suitable ratio with regard to the optimum action in the case of the specific cultivated plant is determined from case to case, i.e. depending on the chloroacetanilide or thiolcarbamate used.

As mentioned above, various methods and techniques can be employed for the use of the novel antidote of formula I together with herbicidal active substances or mixtures of active substances of e.g. the chloroacetanilide class and/or of the thiolcarbamate class. The following are some examples of the methods and techniques which may be used:

1.) Seed dressing.

a) Dressing of the seed with an antidote formulated as a wettable powder by shaking of the constituents in a vessel until there exists a uniform distribution over the surface of the seeds (dry dressing). The amount of antidote used for this purpose is about 10 to 500 g (40 g to 2 kg of wettable powder) per 100 kg of seed.

b) Dressing of the seed with an emulsion concentrate of the antidote by the method and with the amounts given under a) (wet dressing).

c) Dressing by immersion of the seed in a liquor containing 50—3200 ppm of antidote for 1—20 hours and subsequent drying of the seed (immersion dressing).

2.) Application as tank mixture.

A liquid preparation of a mixture of antidote and herbicide (quantitative ratio between 10:1 and 1:10) is used, with the applied amount of herbicide being 0.1 to 10 kg per hectare. This tank mixture is preferably applied before emergence (either before or after sowing), or it is worked into the unsown soil to a depth of 5—10 cm.

3.) Application into the seed furrow.

The antidote is introduced, as an emulsion concentrate, wettable powder or granulate, into the open sown seed furrow and, after the covering of the seed furrow in the normal manner, the herbicide is applied either before or after emergence of the plants.

The antidote can therefore be applied before, together with, or after the herbicide, and its application to the seeds or to the field before emergence can be effected either before or after sowing; or in certain cases it can be effected also after germination of the seed (post-emergence).

If the antidote is applied simultaneously with the herbicide, this may be accomplished by the use of a composition according to the invention, which composition contains the oxime ether of formula I and at least one herbicide, e.g., from the chloroacetanilide and/or thiolcarbamate class, generally together with additives such as carriers and/or distribution agents.

The selective combating of weeds in cultivated crops according to the invention, especially in the *sorghum* and *rice genera*, is such that the seeds of the cultivated plants or the cultivated areas intended for sowing or already sown, or on which the sown plants have already emerged, can be treated, simultaneously, or successively in any desired

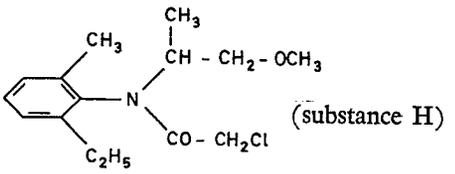
sequence and at a suitable interval of time, on the one hand with phenylglyoxylonitrile-2-oxime-cyanomethyl ether of formula I as the antidote protecting the cultivated plants or the seed thereof, and on the other hand with at least one herbicidal active substance, preferably of the chloroacetanilide class and/or of the thiolcarbamate class.

The compositions used, which contain herbicide and antidote separately or together, can be in any suitable conventional form. They can be produced in a manner known per se, e.g., by the intimate mixing and grinding of the active substance(s) (including antidote) with suitable carriers and/or distributing agents, optionally with the addition of dispersing agents or solvents.

The usual forms of such compositions are either solid, such as dusts, scattering agents and granulates, or liquid, such as solutions and aqueous dispersions; or they are water-dispersible concentrates of active substance, such as wettable powders, emulsion concentrates or pastes.

In addition to the "safener" action of the antidote of formula I according to the invention, there is observed a certain antagonising counteraction moreover on the growth-inhibiting effect of some growth regulators on grasses in the case of overdosage of the growth inhibitor. Furthermore, the compound of formula I, used on its own, exhibits a germination-promoting action on certain seed varieties, such as those of sorghum, rice. The invention accordingly further provides a method for promoting germination of seed of cultivated plants which method comprises treating the seed before or during germination with the oxime ether of the formula I.

The following tests were carried out to determine the selective herbicidal action of a highly effective first-class herbicidal product of the chloroacetanilide class, on its own or together with the antidote of formula I according to the invention; N-[3'-methoxypropyl) - (2')] - 2 - methyl - 6 - ethylchloroacetanilide (DOS 2,328,340) of the formula



(substance H)

was used as the *herbicidal active substance.*

1) Pre-emergence application as tank mixture.

a) After sowing.

Aqueous stock liquors (suspensions) from formulated wettable powders of the herbicide (substance H) and the antidote of formula I (substance S) according to the invention were produced; and these were then applied, both on their own and as mixtures at the given concentrations and in the given mixture ratios, directly after the sowing of various varieties of cultivated millet, namely *Sorghum hybridum* (varieties "Funk," "Dekalb," NK 222" and "DC 59"), in pots or in seed trays in the greenhouse, the said liquors being applied to the surface of the soil in the sown vessels. The pots or seed trays were then kept at 22—23° C with the required amount of watering, and the results were evaluated after 15 days according to the following ratings:

9=plants undamaged (as in the case of the untreated control plants),
1=plants completely destroyed,
2—8=intermediate stages of damage.

b) Before sowing (PPI).

In the same manner as under a), soil in pots and in seed trays was treated with the liquors containing the active substance, and immediately afterwards these vessels were sown with seed of the millet variety "Funk."

The results are summarised in the following Table I. The concentration values in kg/hectare in relation to the other units of measure are as follows:

1 kg/hectare=0.1 g/m^2=2 mg per litre of soil (since seed trays and pots are filled with soil to a depth of 5 cm).

TABLE I

Applied concentration in kg/hectare Substance		Variety of *Sorghum hybridum* before sowing after sowing														
		Funk b			Funk a			Dekal b			NK222			DC59		
H	S	H	H+S	S	H	H+S	S	H	H+S	S	H	H+S	S	H	H+S	S
2.0	4.0	1	9	9												
2.0	2.0	1	9	9												
4.0	16.0				1	8	9	1	8	9	1	9	9	2	9	9
4.0	8.0					6			6			6			6	
2.0	8.0				2	9	9	2	8	9	2	9	9	2	9	9
2.0	4.0					8	9		8	9		9	9		9	9

It is seen that the cultivated millet varieties remain virtually unaffected with the application of various mixture ratios H:S at the different concentrations, whereas with application of the herbicide H alone they are completely destroyed even at low concentrations.

2) Seed dressing (wet).

Aqueous emulsion concentrates (liquid) of the antidote according to the invention were prepared, and the cultivated-millet seed (50 g of seed) in a bottle was treated therewith by shaking. The various concentrations of antidote were expressed in grams of antidote per 100 kg of seed. Shortly after this dressing treatment, the seed was sown in pots or in seed trays and then treated in the usual manner (pre-emergence) as described under a). The results were evaluated 15 days after application of the herbicide using the same ratings as before; the results are listed in the following Table II.

TABLE II

Applied concentration Substance S	Herbicide H	Variety of *Sorghum hybridum*											
		Funk			Dekalb			NK222			DC59		
g/100 kg of seed	kg/hectare	H	H+S	S	H	H+S	S	H	H+S	S	H	H+S	S
150	4	1	8	8	1	5	9	1	5	8	2	5	8
75	4		9	9		7	9		8	9		8	9
37.5	4		9	9		3	9		6	9		7	9
150	2	2	9		2	8		2	8		2	8	
75	2		9			9			9			9	
37.5	2		9			9			9			9	

It is seen here too that substantially complete protection of the cultivated millet is obtained where the concentration of herbicide H is low, but sufficiently high to combat weeds, even with low applied amounts of the antidote S. With higher doses of herbicide the results are somewhat different depending on the variety of cultivated millet used; however, in the case of the "Funk" variety the results are still optimum.

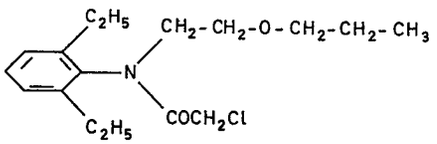
It was possible also in field tests to confirm these excellent results, whereby it was shown that still better results can be obtained with the seed dressing method than with the tank mixture method.

The antagonistic action of the antidote

according to the invention does not however extend to the main weeds normally associated with cultivated plants, e.g. *Echinochloa, Setaria italica, Digitaria sanguinalis.* These weeds are destroyed by the herbicides used with the antidote practically to the same high degree as that resulting without the presence of the antidote.

Also insecticides, fungicides, such as "Diazinon," "Captain" and "Methoxychlor" do not lose their effectiveness as a result of the antidote; such insecticides can therefore be concomitantly used in seed dressing.

Good "safening" effects similar to those resulting with the use of the herbicide H can be obtained when the oxime ether according to the invention is employed with thiolcarbamates and with other chloroacetanilides even on other crops, as is illustrated by the following test with rice where N-[2-n-propyloxyethyl] - 2,6 - diethyl - chloroacetanilide of the formula



is used as the *herbicide* (K).

Rice is grown in very moist soil until the plants carry 3 to 4 leaves. The plants are then taken from the soil and the adhering soil is washed from the roots with water. The roots are thereupon immersed for 30 minutes in aqueous preparations containing respectively 125, 32, 8 and 2 ppm(=parts of active substance per 10^6 parts of the "solution") of the antidote, phenylglyoxylonitrile-2-oxime-cyanomethyl ether.

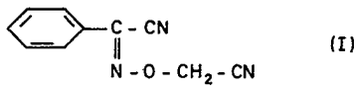
The rice plants treated in this manner are then planted in soil in containers having a surface area of 12 cm × 8 cm and a depth of 15 cm (96 cm^2 surface area and 1.44 litres volume per container). The height of water is subsequently adjusted to 2 cm. Spraying is carried out after 10 days with a 0.4% liquor of the herbicide K [N-2'-n-propyloxyethyl)-2,6-diethyl-N-chloroacetanilide], the equivalent amount of liquor being 500 litres per hectare or *2 kg/hectare* (=0.5 cm^3 of liquor per container). The liquor is sprayed over the leaves of the rice plants and into the water. The test is evaluated 20 days after the treatment with the herbicide. Evaluation is on the basis of the scale of ratings used in the test with millet (9=normal condition; 1=completely destroyed).

The results are summarised in the following table:

Conc. herbicide K	Conc. antidote S	Toxicities on rice		
		K (alone)	K + S	S (alone)
2 kg/ha	125 ppm	4	8	9
2 kg/ha	32 ppm	4	7	9
2 kg/ha	8 ppm	4	8	9
2 kg/ha	2 ppm	4	8	9

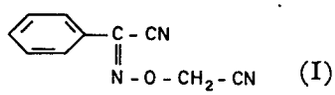
WHAT WE CLAIM IS:—

1. The compound phenylglyoxylonitrile-2-oxime-cyanomethyl ether of formula I



(I)

2. A process for preparing phenylglyoxylonitrile-2-oxime-cyanomethyl ether of formula I



(I)

which process comprises reacting a salt of phenylglyoxylonitrile-2-oxime with a haloacetonitrile.

3. A process according to claim 2 wherein an alkali metal salt of phenylglyoxylonitrile-2-oxime as defined in claim 2 is reacted with a haloacetonitrile.

4. A process for preparing phenylglyoxylonitrile-2-oxime-cyanomethyl ether as defined in claim 1 substantially as described in the Example.

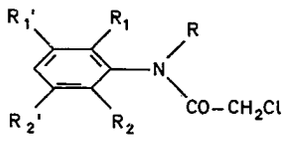
5. Phenylglyoxylonitrile - 2 - oxime - cyanomethyl ether as defined in claim 1 when prepared by the process claimed in any one of claims 2 to 4.

6. A composition for combating weeds in a crop of cultivated plants, which composition contains at least one herbicide as the herbicidally effective ingredient together with the compound phenylglyoxylonitrile-2-oxime-cyanomethyl ether of formula I as defined in claim 1, as crop plant-protecting antidote.

7. A composition according to claim 6 which contains, as herbicidally effective ingredient,

a chloroacetanilide or thiolcarbamate herbicide.

8. A composition according to claim 6, which contains, as herbicidally effective ingredient, a chloroacetanilide of the formula



wherein

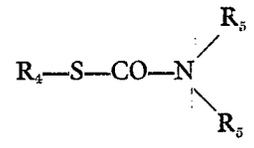
each of R_1, R_1', R_2 and R_2', which may be the same or different, represents a hydrogen or halogen atom, or an alkyl, haloalkyl or alkoxy group having 1 to 4 carbon atoms, or an alkoxyalkyl or alkylthioalkyl group having 1 to 4 carbon atoms in each alkyl moiety, and

R represents an alkyl group having 1 to 4 carbon atoms which is substituted by one or more carboxy, carboxylic acid ester, carboxylic acid amide or cyano groups, or an alkoxyalkyl group of formula —A—O—R_3 (wherein A represents an alkylene group having 1 to 4 carbon atoms of which 1 or 2 are in the direct chain, and R_3 represents an alkyl or alkenyl group having up to 4 carbon atoms or a cycloalkyl or cycloalkylmethyl group having 3 to 6 ring carbon atoms).

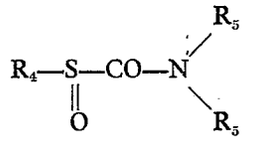
9. A composition according to claim 6 which contains N-[3'-methoxypropyl(2')]-2-methyl - 6 - ethyl - chloroacetanilide as herbicidally effective ingredient.

10. A composition according to claim 6 which contains N-(2'-n-propyloxyethyl)-2,6-diethyl-chloroacetanilide as herbicidally effective ingredient.

11. A composition according to claim 6, which contains, as herbicidally effective ingredient, a thiolcarbamate of the formula



or



wherein R_4 represents an alkyl group having 1 to 4 carbon atoms, and the R_5 groups are the same and represent alkyl groups having 3 or 4 carbon atoms.

12. A composition according to claim 6, which contains the compound N,N-diisobutyl-thioethylcarbamate of the formula

$$C_2H_5—S—CO—N(i\text{-}C_4H_9)_2$$

as herbicidally effective ingredient.

13. A solid composition for use as herbicide antidote which composition comprises, as active ingredient, phenylglyoxylonitrile - 2 - oxime - cyanomethyl ether as defined in claim 1 together with a solid extender and, optionally, a surface active agent.

14. A liquid composition for use as herbicide antidote which composition comprises, as active ingredient, phenylglyoxylonitrile - 2 - oxime - cyanomethyl ether as defined in claim 1 together with a liquid diluent and a surface active agent.

15. A method for selectively combating weeds in a crop of cultivated plants, which method comprises applying to a locus intended for sowing or already sown, or a locus on which the sown plants have already emerged, simultaneously or successively in either order (i) a herbicide and (ii) phenylglyoxylonitrile-2-oxime-cyanomethyl ether as defined in claim 1 in an amount sufficient to protect the emerging or emerged cultivated plants from attack by the herbicide.

16. A method according to claim 15 wherein the ground which is intended for sowing and provided with seed furrows is treated with a concentrated solid or liquid composition containing the phenylglyoxylonitrile - 2 - oxime - cyanomethyl ether and the herbicide is applied, after the seed furrows have been covered, before emergence of the plants.

17. A method according to claim 15 or 16 wherein the cultivated plants are millet or rice plants.

18. A method for selectively combating weeds in a crop of cultivated plants which method comprises dressing seed before sowing with phenylglyoxylonitrile - 2 - oxime-cyanomethyl ether as defined in claim 1 and applying a herbicide to the locus in which the seeds have been sown and before or after germination such as the emerging or emerged cultivated plants are protected from attack by the herbicide.

19. A method according to claim 18 wherein the seed is dressed before sowing by shaking with a concentrated pulverulent or liquid composition of the phenylglyoxylonitrile-2-oximelcyanomethyl ether to give uniform distribution of the phenylglyoxylonitrile-2-oxime-cyanomethyl ether over the surface of the seed, the amount of the composition being such that 10 to 500 g of phenylglyoxylonitrile-2-oxime-cyanomethyl ether per 100 kg of seed is used.

20. A method according to claim 18 or 19 wherein the seed is also dressed with an insecticidal, acaricidal and/or fungicidal and/or nematocidal substance.

21. A method according to any one of

claims 18 to 20 wherein the seed is millet or rice seed.

22. A method according to any one of claims 15 to 21 wherein there is used as herbicide a herbicidally effective ingredient as defined in any one of claims 7 to 12.

23. A method for promoting germination of seed of cultivated plants, which method comprises treating the seed, before or during germination, with phenylglyoxylonitrile-2-oxime-cyanomethyl ether as defined in claim 1.

24. A method according to claim 23 in which the seed is sorghum seed.

25. A method according to claim 23 in which the seed is rice seed.

26. Seed dressed with phenylglyoxylonitrile-2-oxime-cyanomethyl ether as defined in claim 1.

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8, Staple Inn, London, WC1V 7QH.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.