

PATENT SPECIFICATION

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(54) AROMATIC DIURETHANES AND THEIR USE AS SELECTIVE HERBICIDES

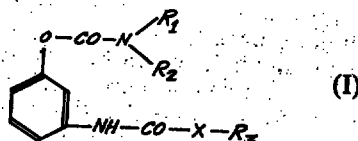
(71) We, SCHERING AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new diurethanes having selective herbicidal properties, which herbicides are especially suitable for combating weeds in cotton crops, with processes for their manufacture, with herbicidal preparations containing them and with their use.

The herbicidal action of diurethanes has been known (cf. German Offenlegungsschriften Nos. 1,567,151 and 1,568,621). These Specifications are, however, preponderantly concerned with selective herbicides for use in beet crops. These herbicides do not possess the requisite selectivity when used against weeds in cotton crops.

The problem upon which the present invention is based has been to provide a weed combating agent that can be used especially in cotton crops, which problem has now been solved by the present invention.

The present invention provides compounds of the general formula I



in which

R_1 represents an *n*-propyl, *n*-butyl, isobutyl or benzyl group,
 R_2 represents an unsubstituted phenyl group or a phenyl group substituted by one or more substituents selected from methyl, ethyl, methoxy and methylmercapto groups and chlorine atoms,

R_3 represents a methyl or ethyl group, and
 X represents an oxygen or sulphur atom.

The compounds of the present invention are distinguished by the fact that cotton in all stages of its development has a surprisingly high tolerability against them, the crop plants not being damaged by the use of the compounds even in the embryo stage. This constitutes an extraordinary technical advance, because weeds can be combated in these crops independently of the crops' stage of development at any time when an optimum attack by the weeds present can be expected. This is not possible with the herbicides based on phenyl-ureas hitherto used for combating weeds in cotton, which can be used only in a stage of growth of the cotton at which the weeds have also strongly developed and are therefore difficult to combat.

The compounds of the present invention are most effective when they are applied in the post-emergence method. In this case the compounds act not only

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against the weeds that have sprouted, but also, owing to their residual action in the soil, attack germinating weed plants, so that a long lasting attack is ensured.

Apart from their use in cotton crops, the compounds of the present invention can also be used for combating weeds in ground-nut crops, rice crops and carrot crops, in which they also have an extraordinary selective action against the weeds while being tolerated by the crops.

5 The herbicidal action of the compounds of the general formula I extends to many kinds of weeds, among which for example, there may be mentioned the following: *Setaria verticillata*, *Amarantus spinosus*, *Datura stramonium*, *Portulaca oleracea*, *Xanthium pensylvanicum*, *Eleusine indica*, *Rottboellia exaltata*, *Sinapis sp.*, *Solanum sp.*, *Stellaria media*, *Senecio vulgaris*, *Lamium amplexicaule*, *Centaurea cyanus*, *Amarantus retroflexus*, *Galium aparine*, *Chrysanthemum segetum*, *Echinochloa crus galli*, *Setaria italica*, *Ipomoea purpurea*, *Polygonum papathifolium*, *Digitaria sanguinalis* and *Setaria faberi*.

10 The rates of application for a selective weed control are approximately 0.5 to 5 kg of active substance per hectare; when two or more compounds of the general formula I are used the range of approximately 0.5 to 5 kg refers of course to the total amount applied of these compounds. These rates of application may, if desired, be increased to 10 kg of active substance per hectare without substantially injuriously affecting the crop plants.

15 The present invention accordingly also provides a herbicidal preparation which comprises a compound of the general formula I, in admixture or conjunction with a suitable carrier. The preparation may of course contain one or more compounds of the general formula I.

20 The present invention further provides a method of protecting a living plant against weeds, wherein the area in the vicinity of a living plant is treated with a compound of the general formula I.

25 The present invention further provides a method of protecting a crop area against weeds, wherein a crop area is treated with a compound of the general formula I.

30 The compounds of the present invention can be used either singly as the sole active substance, or in admixture with one another or in admixture with other active substances. If desired, there may be added other plant protecting agents or pest combating agents, for example fungicides, nematicides or other agents, depending on the result desired. Fertilizers may also be added.

35 When it is desired to widen the spectrum of action there may also be added other herbicides, but, depending on the nature of the component added, the selectivity is not always maintained. As herbicidally active co-components of such mixtures there are suitable, for example, active substances belonging to the groups of carbamide acid esters and thiocarbamide acid esters, substituted anilines and anilides, triazines, amino-triazoles, diazines, for example uracils, for example 3-cyclohexyl-5-trimethylene-uracil, 1-phenyl-4-amino-5-chloropyridazone-(6), aliphatic carboxylic acids and halogen-carboxylic acids, halogenated benzoic acids and phenyl-acetic acids, aryloxy-carboxylic acids, hydrazides, amides, nitriles, halogen-carboxylic acids, for example 2,2-dichloropropionic acid or salts thereof, and tetrafluoropropionic acid or salts thereof, esters of such carboxylic acids, ureas, 2,3,6-trichlorobenzoyloxy-propanol, agents containing thiocyanogen and other compounds.

40 Depending on the purpose of use other substances may be added, among which there are also included, for example, non-phytotoxic additions, which in combination with herbicides may give a synergistic increase in action, for example wetting agents, emulsifiers, solvents and oily additions.

45 The active compounds of the present invention are advantageously used in the form of herbicidal preparations, for example powders, spraying or dusting agents, granules, solutions, emulsions or suspensions, with the addition of liquid and/or solid vehicles or diluents, and, if desired, of surface-active agents, for example wetting, adherent, emulsifying and/or dispersing agents.

50 Suitable liquid carriers are, for example, water, aliphatic and aromatic hydrocarbons, for example benzene, toluene and xylene, cyclohexanone and isophorone, and also mineral oil fractions.

55 As solid carriers there are suitable mineral earths, for example tonsil, silica gel, talcum, kaolin, attaclay, limestone and silicic acid, and vegetable products, for example meals.

60 As surface-active agents there may be mentioned, for example, calcium lignin sulphonate, polyoxyethylene octylphenol ethers, naphthalene sulphonic acid,

phenol sulphonic acids, formaldehyde condensates, fatty alcohol sulphates and alkali metal and alkaline earth metal salts of fatty acids.

It has been surprisingly found that the herbicidal action and the selectivity of the preparations can be increased, when they contain the surface-active agents in proportions that exceed the usual quantities.

The total amount of the active compound or compounds of the present invention in the various herbicidal preparations may vary within wide limits. The preparations may contain, for example, 20 to 80 per cent by weight of active compound(s), 80 to 20 per cent by weight of liquid or solid carrier, and, if desired, also up to 30 per cent by weight of surface-active agent(s).

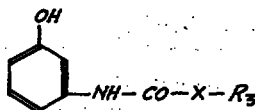
The active compounds may be applied in the usual manner, for example, with water as carrier in quantities of spray liquor from 100 to 1,000 litres per hectare. For the total destruction of weeds it may be necessary in some cases to apply quantities of spray liquor exceeding 1,000 litres per hectare. It is also possible to use the active compounds in the so-called "Ultra-low-Volume method", and also to apply them in the form of the so-called microgranules.

These preparations may be prepared in a manner *per se*, for example, by mixing or grinding methods. If desired, the individual components may be mixed together only shortly before being used, for example, in the so-called tank mix method carried out in practice.

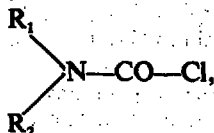
The new compounds of the present invention may be prepared by methods known *per se*, for example by one of the following processes which are also included within the scope of the present invention.

The present invention accordingly further provides a process for the manufacture of a compound of the general formula I, wherein

a) a compound of the general formula

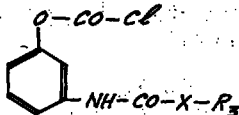


in which R_3 and X have the meanings given above, or an alkali metal salt thereof is reacted with a carbamoyl chloride of the general formula

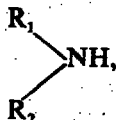


in which R_1 and R_2 have the meanings given above, if desired in the presence of a tertiary organic base, for example triethylamine or pyridine, at a temperature of 0°C to 100°C , or

b) a compound of the general formula

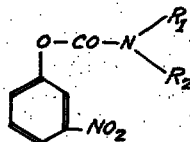


in which R_3 and X have the meanings given above, is reacted in the presence of an acid-binding agent, for example an inorganic base, for example sodium hydroxide solution, sodium carbonate or potassium carbonate, or a tertiary organic base, for example triethylamine, with an amine of the general formula

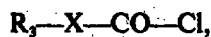


in which R_1 and R_2 have the meanings given above, or

c) a nitro compound of the general formula



in which R_1 and R_2 have the meanings given above, is catalytically hydrogenated, for example, with the use of nickel in methanol, to form the corresponding amine which is then reacted in the presence of an acid-binding agent, for example an inorganic base, for example sodium hydroxide solution, sodium carbonate or potassium carbonate, or an organic base, for example triethylamine, with a compound of the general formula



in which R_3 and X have the meanings given above.

The products of the process of the present invention are isolated in the usual manner.

Some compounds of the present invention are listed in the following Table.

TABLE I

Compound number	Name of the compound	Physical constant
1	Methyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	M.p.: 128 – 129°C
2	Ethyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	M.p.: 100 – 101°C
3	Methyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	M.p.: 82 – 85°C
4	Ethyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	$n_D^{20} = 1.5349$
5	Methyl-N-[3-[N-isobutyl-N-(3-methylphenyl)-carbamoyloxy]-phenyl]-carbamate	M.p.: 76 – 80°C
6	Ethyl-N-[3-[N-isobutyl-N-(3-methylphenyl)-carbamoyloxy]-phenyl]-carbamate	M.p.: 79 – 80°C
7	S-Methyl-N-[3-[N-isobutyl-N-(3-methylphenyl)-carbamoyloxy]-phenyl]-thiocarbamate	M.p.: 119 – 121°C
8	Methyl-N-[3-(N-phenyl-N-benzyl-carbamoyloxy)-phenyl]-carbamate	M.p.: 83 – 86°C
9	S-Methyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	M.p.: 96 – 98°C
10	S-Methyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	M.p.: 83 – 85°C

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TABLE I (Continued)

Compound number	Name of the compound	Physical constant
11	Methyl-N-[3-(N-propyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	M.p.: 97 – 98°C
12	Ethyl-N-[3-(N-propyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	M.p.: 105 – 106°C
13	S-Methyl-N-[3-(N-propyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	M.p.: 94 – 96°C
14	Methyl-N-[3-[N- <i>n</i> -butyl-N-(4-ethylphenyl)-carbamoyloxy]-phenyl]-carbamate	M.p.: 73 – 76°C
15	S-Methyl-N-[3-(N-benzyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	M.p.: 129 – 131°C
16	Ethyl-N-[3-(N-benzyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	M.p.: 83 – 85°C
17	S-Ethyl-N-[3-(N- <i>n</i> -butyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	M.p.: 85 – 87°C
18	S-Methyl-N-[3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	M.p.: 120 – 123°C
19	S-Methyl-N-[3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	M.p.: 103 – 104°C
20	Methyl-N-[3-[N-(3-methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl]-carbamate	M.p.: 87 – 88°C
21	Methyl-N-[3-[N- <i>n</i> -butyl-N-(3-methoxyphenyl)-carbamoyloxy]-phenyl]-carbamate	M.p.: 74 – 75°C
22	S-Methyl-N-[3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	M.p.: 101 – 102°C
23	S-Methyl-N-[3-[N-(4-ethylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	M.p.: 96 – 97°C
24	S-Methyl-N-[3-[N-(3-Methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	M.p.: 103 – 105°C
25	Methyl-N-[3-[N-(4-ethylphenyl)-N-propyl-carbamoyloxy]-phenyl]-carbamate	$n_D^{20} = 1.5487$
26	S-Methyl-N-[3-[N- <i>n</i> -butyl-N-(3-methoxyphenyl)-carbamoyloxy]-phenyl]-thiocarbamate	M.p.: 106 – 107°C

TABLE I (Continued)

Compound number	Name of the compound	Physical constant
27	Ethyl-N-{3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	$n_D^{20} = 1.5472$
28	Ethyl-N-{3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	M.p.: 85 – 87°C
29	Ethyl-N-{3-[N-(4-ethylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	$n_D^{20} = 1.5436$
30	Ethyl-N-{3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	M.p.: 88 – 89°C
31	Ethyl-N-{3-[N-(3-methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	M.p.: 93 – 94°C
32	S-Ethyl-N-{3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	M.p.: 84 – 86°C
33	Ethyl-N-{3-[N- <i>n</i> -butyl-N-(3-methoxyphenyl)-carbamoyloxy]-phenyl}-carbamate	M.p.: 72 – 73°C
34	S-Ethyl-N-{3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	M.p.: 111 – 113°C
35	S-Ethyl-N-{3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	$n_D^{20} = 1.5617$
36	S-Ethyl-N-{3-[N-(3-methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	M.p.: 88 – 89°C
37	S-Ethyl-N-{3-[N- <i>n</i> -butyl-N-(3-methoxyphenyl)-carbamoyloxy]-phenyl}-thiocarbamate	M.p.: 66 – 68°C
38	Methyl-N-{3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	
39	Methyl-N-{3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	
40	Methyl-N-{3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	

These compounds are readily soluble in acetone, cyclohexanone, ethyl acetate, isophorone, ether and tetrahydrofuran, and are practically insoluble in water and light gasoline.

Among the compounds of the present invention, the compounds numbered 1, 2, 3, 4, 7, 9, 10, 11, 12 and 13 in the above Table are excellent herbicides in cotton, carrot, ground-nut and rice crops.

Attention is directed under Section 9 to our U.K. Patent Specification No. 1,369,491.

The following Examples illustrate the invention. Examples 1 and 2 illustrate the manufacture of compounds of the present invention and Examples 3 and 4 illustrate the herbicidal activity of compounds of the present invention.

Example 1.

Methyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate (Compound No. 1)

Into a mixture of 14.9 grams of N-isobutyl-aniline, 50 ml of water and 30 ml of ethyl acetate there were added dropwise, while stirring, at 10 to 15°C a solution of 22.9 grams of chloroformic acid-3-(N-carbomethoxyamino)-phenyl ester in 50 ml of ethyl acetate and simultaneously a solution of 13.8 grams of potassium carbonate in 50 ml of water. The whole was further stirred for 30 minutes while cooling with ice, and the organic phase was then separated and washed at 0°C with a small amount of a dilute aqueous solution of sodium hydroxide. After being dried with magnesium sulphate, the solution was concentrated under reduced pressure and pentane was added to the evaporation residue, whereupon the reaction product crystallized out.

Yield: 23.3 grams=68% of the theoretical yield.

M.p.: 128 to 129°C.

Example 2.

Ethyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate (Compound No. 2)

The sodium salt prepared from 16.7 grams of 3-hydroxy-carbanilic acid methyl ester and sodium methylate (from 2.3 grams of sodium) in absolute methanol was, after thorough removal of the methanol, suspended *in vacuo* in 100 ml of dry methyl isobutyl ketone. There was introduced dropwise while stirring at 70°C a solution of 21.2 grams of N-isobutyl-N-phenylcarbamoyl chloride in 50 ml of dry methyl isobutyl ketone, and the whole was further stirred for 45 minutes at this temperature. The whole was then cooled to 0°C, and washed at this temperature with a small amount of a dilute aqueous solution of sodium hydroxide. After drying the mixture with magnesium sulphate, it was concentrated under reduced pressure and ether was added to the residue, whereupon the reaction product crystallized out.

Yield: 23.1 grams=65% of the theoretical yield.

M.p.: 100 to 101°C.

The other compounds listed in Table I above can be prepared in an analogous manner.

Example 3.

The plants listed in the following Table were treated in a greenhouse by the post-emergence method in a series of tests with preparations used in such amounts that 3 kg of the active substances were in each case applied in the form of an aqueous emulsion using 500 litres of water per hectare at an early stage in the development of the plants. The evaluation was carried out 14 days after the treatment according to a scale of classification extending from 0 representing "totally destroyed" to 10 representing "not damaged".

The results demonstrate the much better selectivity and anti-weed action of the compounds of the present invention as compared with those of the known agents.

Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare									
Methyl-N-[3-(N- <i>n</i> -butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	0	0	0	0	0	0
Ethyl-N-[3-(N- <i>n</i> -butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	0	0	0	0	0	0
Methyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	0	0	0	0	0	0
Methyl-N-[3-(N-isobutyl-N-(3-methylphenyl)-carbamoyloxy)-phenyl]-carbamate	3	10	—	0	0	0	0	0	0	0
Ethyl-N-[3-(N-isobutyl-N-(3-methylphenyl)-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	0	0	0	0	0	0
S-Methyl-N-[3-(N-isobutyl-N-(3-methylphenyl)-carbamoyloxy)-phenyl]-thiocarbamate	3	10	10	0	0	0	0	0	0	0

Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare									
Methyl-N-[3-(N-phenyl-N-benzyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	0	-	0	0	0	0
Ethyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	1	0	0	0	0	0
S-Methyl-N-[3-(N-isobutyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	3	10	10	0	0	0	0	0	0	0
S-Methyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	3	10	10	0	0	0	0	0	1	0
Methyl-N-[3-(N-propyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	0	0	0	0	0	0
Ethyl-N-[3-(N-propyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	0	0	0	0	0	0
S-Methyl-N-[3-(N-propyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	3	-	10	0	0	0	0	0	0	0

Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare													
S-Methyl-N-[3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	3	-	9	0	0	0	0	0	0	0	0	0	0	0
S-Methyl-N-[3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	3	-	9	0	0	0	0	0	0	0	0	0	0	0
Methyl-N-[3-[N-(3-methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl]-carbamate	3	8	10	0	0	0	5	4	0	0	1	0	2	0
Methyl-N-[3-[N-n-butyl-N-(3-phenyl)-carbamoyloxy]-phenyl]-carbamate	3	9	10	0	0	0	4	7	0	0	0	0	3	0
S-Methyl-N-[3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	3	-	10	0	0	0	0	0	0	0	0	0	2	0
S-Methyl-N-[3-[N-(4-ethylphenyl)-N-propyl-carbamoyloxy]-phenyl]-thiocarbamate	3	-	9	0	0	0	0	0	0	0	0	0	4	1

Cotton

Ground-nut

*Polygonum lapathifolium**Stellaria media**Senecio vulgaris**Lamium amplexicaule**Centaurea cyanus**Amarantus retroflexus**Chrysanthemum segetum**Ipomoea purpurea**Echinochloa crus galli**Setaria italica**Digitaria sanguinalis**Setaria faberi*

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1,467,371

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Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare												
S-Methyl-N-{3-[N-(3-methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	3	-	10	0	0	0	0	0	0	0	0	1	0
Methyl-N-{3-[N-(4-ethylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	-	10	0	0	0	0	0	0	0	0	6	0
S-Methyl-N-{3-[N-n-butyl-N-(3-methoxyphenyl)-carbamoyloxy]-phenyl}-thiocarbamate	3	-	10	0	0	0	0	0	0	0	0	6	0
Ethyl-N-{3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	10	10	0	0	0	0	0	0	1	0	6	0
Ethyl-N-{3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	10	10	0	0	0	0	0	0	0	0	4	0
Ethyl-N-{3-[N-(4-ethylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	-	10	0	0	0	0	1	0	0	0	5	0

Rate of application in kg of active substance per hectare

Cotton

Ground-nut

Polygonum lapathifolium

Stellaria media

Senecio vulgaris

Lamium amplexicaule

Centaurea cyanus

Amarantus retroflexus

Chrysanthemum segetum

Ipomoea purpurea

Echinochloa crus galli

Setaria italica

Digitaria sanguinalis

Setaria faberi

Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare													
Ethyl-N-{3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	1	10	0	0	0	0	0	0	0	0	0	0	0
Ethyl-N-{3-[N-(3-methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	10	10	0	0	0	0	1	0	0	4	1	6	0
S-Ethyl-N-{3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	3	9	10	0	0	0	0	0	0	0	0	0	0	0
Ethyl-N-{3-[N-n-butyl-N-(3-methoxyphenyl)-carbamoyloxy]-phenyl}-carbamate	3	9	9	1	0	0	0	3	0	2	1	2	2	0
S-Ethyl-N-{3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	3	9	10	1	1	1	0	0	0	0	0	2	1	1
S-Ethyl-N-{3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	3	9	10	0	0	0	0	3	0	0	0	0	0	1

Cotton

Ground-nut

*Polygonum lapathifolium**Stellaria media**Senecio vulgaris**Lamium amplexicaule**Centaurea cyamus**Amarantus retroflexus**Chrysanthemum segetum**Ipomoea purpurea**Echinochloa crus galli**Setaria italica**Digitaria sanguinalis**Setaria faberi*

Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare													
S-Ethyl-N-{3-[N-(3-methoxyphenyl)-N-propyl-carbamoyloxy]-phenyl}-thiocarbamate	3	10	10	0	0	4	5	0	0	0	0	0	0	1
S-Ethyl-N-{3-[N-n-butyl-N-(3-methoxyphenyl)-carbamoyloxy]-phenyl}-thiocarbamate	3	10	10	1	0	7	7	2	0	0	0	0	0	2
Methyl-N-{3-[N-(2-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	—	10	0	0	0	1	0	0	0	0	1	0	0
Methyl-N-{3-[N-(3-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	—	10	0	0	0	0	0	0	0	0	2	0	0
Methyl-N-{3-[N-(4-methylphenyl)-N-propyl-carbamoyloxy]-phenyl}-carbamate	3	—	8	0	0	0	0	0	0	0	0	4	0	4
Methyl-N-{3-[N-n-butyl-N-(4-ethylphenyl)-carbamoyloxy]-phenyl}-carbamate	3	10	10	0	0	—	1	0	0	0	0	0	0	0

Rate of application in kg of active substance per hectare

Cotton

Ground-nut

Polygonum lapathifolium

Stellaria media

Senecio vulgaris

Lamium amplexicaule

Centaurea cyanus

Amarantus retroflexus

Chrysanthemum segetum

Ipomoea purpurea

Echinochloa crus galli

Setaria italica

Digitaria sanguinalis

Setaria faberi

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Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare					
S-Methyl-N-[3-(N-benzyl-N-phenyl-carbamoyloxy)-phenyl]-thiocarbamate	3	10	10	0	0	0
Ethyl-N-[3-(N-benzyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	3	10	10	0	1	-
<u>Compound in preparation used for comparison</u>						
N-(3-Trifluoromethylphenyl)-N,N-dimethyl-urea	3	0	1	0	0	0
Methyl-N-[3-[N-(3-methylphenyl)-carbamoyloxy]-phenyl]-carbamate	3	5	2	8	-	2

10 = not damaged
0 = totally destroyed

Example 4.

In a greenhouse the plants listed in the following Table in an early stage of development were treated in a series of tests with preparations used in such amounts that 32 kg of the active substance being tested was applied per hectare. The active substances were in each case applied in the form of an aqueous emulsion using 500 litres of water per hectare. 14 Days after the treatment the evaluation was carried out as described in Example 3.

Even at this rate of application the compounds of the present invention still exhibit an excellent herbicidal action.

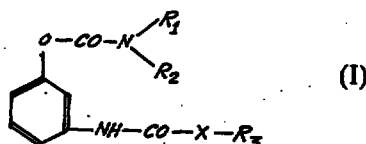
Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare	<i>Amarantus spinosus</i>	<i>Xanthium pensylvanicum</i>	<i>Portulaca oleracea</i>	<i>Setaria verticillata</i>	<i>Rottboellia exaltata</i>	<i>Eleusine indica</i>
Methyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	2	0	0	0	0	1	2
Ethyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	2	0	0	0	0	—	—

0 = totally destroyed

10 = not damaged

WHAT WE CLAIM IS:—

1. A compound of the general formula I



in which

R_1 represents an *n*-propyl, *n*-butyl, isobutyl or benzyl group,
 R_2 represents an unsubstituted phenyl group or a phenyl group substituted by one or more substituents selected from methyl, ethyl, methoxy and methylmercapto groups and chlorine atoms,

R_3 represents a methyl or ethyl group, and

X represents an oxygen or sulphur atom.

2. Methyl - N - [3 - (N - *n* - butyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate.

3. Ethyl - N - [3 - (N - *n* - butyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate.

4. Methyl - N - [3 - (N - isobutyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate.

5. Ethyl - N - [3 - (N - isobutyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate.

6. S - Methyl - N - [3 - (N - isobutyl - N - (3 - methylphenyl) - carbamoyloxy) - phenyl]-thiocarbamate.

7. S - Methyl - N - [3 - (N - isobutyl - N - phenyl - carbamoyloxy) - phenyl]-thiocarbamate.

8. S - Methyl - N - [3 - (N - *n* - butyl - N - phenyl - carbamoyloxy) - phenyl]-thiocarbamate.



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Example 4.

In a greenhouse the plants listed in the following Table in an early stage of development were treated in a series of tests with preparations used in such amounts that 32 kg of the active substance being tested was applied per hectare. The active substances were in each case applied in the form of an aqueous emulsion using 500 litres of water per hectare. 14 Days after the treatment the evaluation was carried out as described in Example 3.

Even at this rate of application the compounds of the present invention still exhibit an excellent herbicidal action.

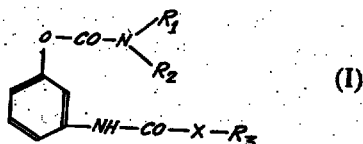
Compound of the present invention in the preparation	Rate of application in kg of active substance per hectare	<i>Amarantus spinosum</i>	<i>Xanthium pensylvanicum</i>	<i>Portulaca oleracea</i>	<i>Setaria verticillata</i>	<i>Rotibollia exaltata</i>	<i>Eleusine indica</i>
Methyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	2	0	0	0	0	1	2
Ethyl-N-[3-(N-n-butyl-N-phenyl-carbamoyloxy)-phenyl]-carbamate	2	0	0	0	0	-	-

0 = totally destroyed

10 = not damaged

WHAT WE CLAIM IS:—

1. A compound of the general formula I



in which

R₁ represents an n-propyl, n-butyl, isobutyl or benzyl group,
R₂ represents an unsubstituted phenyl group or a phenyl group substituted by one or more substituents selected from methyl, ethyl, methoxy and methylmercapto groups and chlorine atoms,

R₃ represents a methyl or ethyl group, and
X represents an oxygen or sulphur atom.

2. Methyl - N - [3 - (N - n - butyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate,

3. Ethyl - N - [3 - (N - n - butyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate,

4. Methyl - N - [3 - (N - isobutyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate,

5. Ethyl - N - [3 - (N - isobutyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate,

6. S - Methyl - N - [3 - (N - isobutyl - N - (3 - methylphenyl) - carbamoyloxy) - phenyl]-thiocarbamate,

7. S - Methyl - N - [3 - (N - isobutyl - N - phenyl - carbamoyloxy) - phenyl]-thiocarbamate,

8. S - Methyl - N - [3 - (N - n - butyl - N - phenyl - carbamoyloxy) - phenyl]-thiocarbamate.



9. Methyl - N - [3 - (N - propyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate.

10. Ethyl - N - [3 - (N - propyl - N - phenyl - carbamoyloxy) - phenyl]-carbamate.

11. S - Methyl - N - [3 - (N - propyl - N - phenyl - carbamoyloxy)-phenyl]-thiocarbamate.

12. A herbicidal preparation which comprises a compound of the general formula I given in claim 1, in which R₁, R₂, R₃ and X have the meanings given in claim 1, in admixture or conjunction with a suitable carrier.

13. A herbicidal preparation which comprises the compound claimed in any one of claims 2 to 11, in admixture or conjunction with a suitable carrier.

14. A herbicidal preparation which comprises any one of the compounds numbered 5, 6, 8 and 14 to 40 in Table I herein, in admixture or conjunction with a suitable carrier.

15. A preparation as claimed in any one of claims 12 to 14, which is in the form of a powder, a spraying or dusting agent, granules, a solution, an emulsion or a suspension.

16. A preparation as claimed in any one of claims 12 to 15, containing a single compound of the general formula I in an amount of 20 to 80% by weight.

17. A preparation as claimed in any one of claims 12 to 15, containing two or more compounds of the general formula I in a total amount of 20 to 80% by weight.

18. A preparation as claimed in any one of claims 12 to 17, containing a single surface-active agent in an amount of up to 30% by weight.

19. A preparation as claimed in any one of claims 12 to 17, containing two or more surface-active agents in a total amount of up to 30% by weight.

20. Any one of the herbicidal preparations as claimed in claim 12 and substantially as described in Example 3 herein.

21. Either one of the herbicidal preparations as claimed in claim 12 and substantially as described in Example 4 herein.

22. A method of protecting a living plant against weeds, wherein the area in the vicinity of a living plant is treated with a compound of the general formula I given in claim 1, in which R₁, R₂, R₃ and X have the meanings given in claim 1.

23. A method as claimed in claim 22 wherein the area is treated with the compound claimed in any one of claims 2 to 11.

24. A method as claimed in claim 22, wherein the area is treated with any one of the compounds numbered 5, 6, 8 and 14 to 40 in Table I herein.

25. A method as claimed in claim 22, wherein the area is treated with a herbicidal preparation as claimed in any one of claims 12 to 21.

26. A method as claimed in any one of claims 22 to 25, wherein a single compound of the general formula I is used for the treatment in an amount of approximately 0.5 to 5 kg per hectare.

27. A method as claimed in any one of claims 22 to 25, wherein two or more compounds of the general formula I are used for the treatment in a total amount of approximately 0.5 to 5 kg per hectare.

28. A method as claimed in any one of claims 22 to 27, wherein the treatment is carried out at the post-emergence stage of the weeds.

29. A method as claimed in claim 22, conducted substantially as described in Example 3 herein.

30. A method of protecting a crop area against weeds, wherein a crop area is treated with a compound of the general formula I given in claim 1, in which R₁, R₂, R₃ and X have the meanings given in claim 1.

31. A method as claimed in claim 30, wherein the crop area is treated with the compound claimed in any one of claims 2 to 11.

32. A method as claimed in claim 30, wherein the crop area is treated with any one of the compounds numbered 5, 6, 8 and 14 to 40 in Table I herein.

33. A method as claimed in claim 30, wherein the crop area is treated with a herbicidal preparation as claimed in any one of claims 12 to 21.

34. A method as claimed in any one of claims 30 to 33, wherein a single compound of the general formula I is used for the treatment in an amount of approximately 0.5 to 5 kg per hectare.

35. A method as claimed in any one of claims 30 to 33, wherein two or more compounds of the general formula I are used for the treatment in a total amount of approximately 0.5 to 5 kg per hectare.

36. A method as claimed in any one of claims 30 to 35, wherein the treatment is carried out at the post-emergence stage of the weeds.



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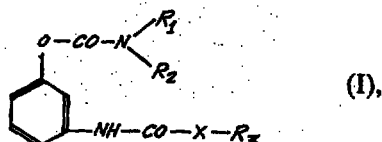
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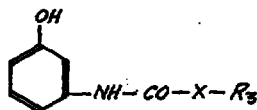
37. A method as claimed in any one of claims 30 to 36, wherein the crop is a cotton crop.

38. A method as claimed in any one of claims 30 to 36, wherein the crop is a carrot, ground-nut or rice crop.

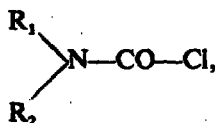
39. A process for the manufacture of a compound of the general formula I



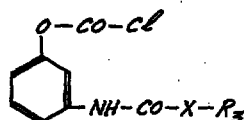
in which R_1 , R_2 , R_3 and X have the meanings given in claim 1, wherein
(a) a compound of the general formula



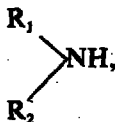
in which R_1 and X have the meanings given above, or an alkali metal salt thereof is reacted with a carbamoyl chloride of the general formula



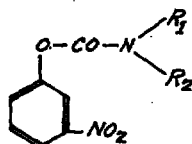
in which R_1 and R_2 have the meanings given above, or
(b) a compound of the general formula



in which R_3 and X have the meanings given above, is reacted in the presence of an acid-binding agent with an amine of the general formula



in which R_1 and R_2 have the meanings given above, or
(c) a nitro compound of the general formula



in which R_1 and R_2 have the meanings given above, is catalytically hydrogenated to form the corresponding amine which is then reacted in the presence of an acid-binding agent with a compound of the general formula



in which R_3 and X have the meanings given above.



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40. A process as claimed in claim 39, wherein the reaction with the carbamoyl chloride is carried out in the presence of a tertiary organic base.

41. A process as claimed in claim 39, conducted substantially as described in Example 1 or 2 herein.

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