

PATENT SPECIFICATION

(11) 1 300 094

NO DRAWINGS

(21) Application No. 2703/70 (22) Filed 20 Jan. 1970

(31) Convention Application No. P 19 03 817.6

(32) Filed 22 Jan. 1969 in

(33) Germany (DT)

(45) Complete Specification published 20 Dec. 1972

(51) International Classification A01N 9/20, 17/00

(52) Index at acceptance

A5E 1A2N1 1A2N4 1A2P 1A3B 1A3C 1A5B3 1C14
1C15D1 1C15D3 1C15E 1C5E 1C5J

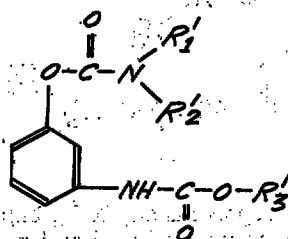


(54) HERBICIDAL PREPARATIONS AND THEIR USE

(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 stabilized, liquid herbicidal preparations containing meta-biscarbamates and with their use.

It has been known that biscarbamates of the general formula,



in which R₁ represents an alkyl group, a cycloalkyl group or an aryl group which may be substituted by one or more substituents selected from halogen atoms, alkyl groups and trifluoromethyl groups and R₂ represents a hydrogen atom or an alkyl group or R₁, and R₂, together with the adjacent nitrogen atom represent a heterocyclic group which may contain further nitrogen and/or oxygen atoms, and R₃ represents an alkyl, alkenyl or alkynyl group which may be terminally substituted by halogen, have good herbicidal properties (cf. Belgian Patent Specification No. 679,283).

Among these active substances those have been especially accepted in practice in which R₂ in the above general formula represents a hydrogen atom, for example (3-methoxycarbonylamino-phenyl) - N - (3 - methyl-phenyl) - carbamate. They are preferably used as liquid preparations which contain apart [Price 25p]

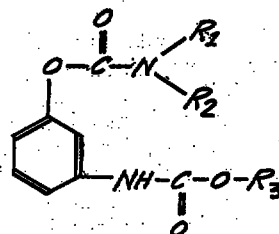
from the active substance at least one organic solvent and at least one surface-active agent as essential ingredients.

However, such liquid preparations have the disadvantage that they are not sufficiently stable and undergo a varying degree of decomposition during storage. As a result, the concentration of active substance is not constant leading to a diminished activity in use.

From United States Patent Specification No. 2,954,396 a process has been known for stabilizing N-substituted alkylcarbamates against hydrolytic decomposition and the following stabilizers have been proposed: acetic acid, phosphoric acid, hydrochloric acid, ammonium dihydrogen phosphate, ammonium chloride, ferric chloride and mixtures of these compounds.

However, in so far as they are soluble at all in the relevant liquid preparations containing meta-biscarbamates, these stabilizers produce no or only insufficient stabilization in such liquid preparations.

The present invention provides a liquid herbicidal preparation which comprises a biscarbamate of the general formula I



(I),

in which R₁ represents an alkyl group, a cycloalkyl group, an unsubstituted aryl group or an aryl group substituted by one or more substituents selected from halogen atoms, alkyl groups and trifluoromethyl groups, R₂ represents a hydrogen atom and R₃ represents an unsubstituted or a terminally halogeno-substituted alkyl, alkenyl or alkynyl group, an organic solvent, a surface-active agent and a

stabilizer selected from aliphatic dicarboxylic acids, aliphatic hydroxycarboxylic acids, nitro-substituted aromatic monocarboxylic acids, aromatic dicarboxylic acids, aliphatic sulphonic acids and aromatic sulphonic acids.

If desired, the liquid herbicidal preparations of the present invention may contain one, two or more of each of the biscarbamates as defined above (that is of the general formula I), one, two or more organic solvents, one, two or more surface-active agents and one, two or more stabilizers selected from aliphatic dicarboxylic acids, aliphatic hydroxycarboxylic acids, nitro-substituted aromatic monocarboxylic acids, aromatic dicarboxylic acids, aliphatic sulphonic acids and aromatic sulphonic acids.

The herbicidal preparations of the present invention are satisfactorily stabilized by the addition of at least one of the organic acids specified. When used in a concentration ranging from 0.05 to 5, preferably from 0.25 to 1.0, % by weight these organic acids develop a good stabilizing activity. In this manner losses in activity of the liquid preparations after prolonged storage are substantially obviated over considerable periods of time or at least they are considerably reduced.

Particularly suitable stabilizing agents are oxalic acid, malonic acid, maleic acid, glycollic acid, lactic acid, citric acid, phthalic acid, 5-nitroisophthalic acid, 2-nitrobenzoic acid, 3,5-dinitrobenzoic acid, 4-chloro-3-nitrobenzoic acid, 2-chloro-3,5-dinitrobenzoic acid, methanesulphonic acid, benzenesulphonic acid, para-toluenesulphonic acid and tetrapropylenebenzenesulphonic acid.

The liquid preparations to be stabilized have the composition normally employed for agents used in plant protection: as their essential ingredients there may especially be mentioned:

(1) The biscarbamates of the above general formula especially (3-methoxycarbonylamino-phenyl)-N-(2-methyl-phenyl)-carbamate, as active ingredient;

(2) solvents, for example aromatic hydrocarbons, cyclohexanone, isophorone, methylhexalin, dibutylphthalate, tetralin, dimethylsulphoxide and dimethylformamide; and

(3) surface-active agents, for example polyethoxylated amines, alcohols, acids and alkylphenols and salts of alkylated benzenesulphonic and naphthalenesulphonic acids.

The concentration of these essential ingredients (1), (2) and (3) in the liquid preparations may be approximately as follows:

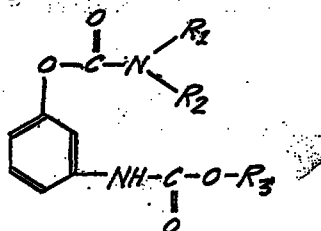
5—50, preferably 10—25, % by weight of active substance,
10—90, preferably 50—80, % by weight of solvent and
2—40, preferably 10—25, % by weight of surface-active agent.

The liquid herbicidal preparations of the present invention are suitable for use as herbicides in controlling undesired plant growth. These herbicides are especially suitable for the selective weed control in the cultivation of some commercial plants, for example sugarbeets and rice. When so used, the stabilizers present in the herbicidal preparations of this invention have no harmful effects.

Accordingly, the present invention also provides a method of selectively controlling weeds in a crop area, wherein a crop area is treated with a liquid herbicidal preparation of the present invention.

The liquid preparations of the present invention are manufactured by simply mixing the aforesaid ingredients together.

The present invention further provides a preparation for use in making a liquid herbicidal preparation according to the present invention, which comprises (a) a biscarbamate of the general formula I



(I),

in which R_1 represents an alkyl group, a cycloalkyl group, an unsubstituted aryl group or an aryl group substituted by one or more substituents selected from halogen atoms, alkyl groups and trifluoromethyl groups, R_2 represents a hydrogen atom and R_3 represents an unsubstituted or a terminally halogeno-substituted alkyl, alkenyl or alkynyl group.

(b) a stabilizer selected from aliphatic dicarboxylic acids, aliphatic hydroxycarboxylic acids, nitro-substituted aromatic monocarboxylic acids, aromatic dicarboxylic acids, aliphatic sulphonic acids and aromatic sulphonic acids and, if desired,

(c) a surface-active agent.

The following Examples illustrate the invention:

Example 1:
A series of liquid preparations having the following composition were prepared:

5	12.5 % by weight of	(3 - methoxycarbonyl-amino - phenyl - N-(3 - methyl - phenyl)-carbamate
10	15.8 % " " "	emulsifier (a mixture of an alkylbenzene-sulphonate, a polyethoxylated fatty acid and a polyethoxylated alkylphenol)
15	2.3 % " " "	a mixture of high-boiling aromatic hydrocarbons

68.4 % " " " isophorone and
1.0 % " " " the stabilizer indicated in Table I below

and stored in glass bottles at + 70°C. After the periods of time shown in the following Table samples were taken and subjected to a thin-layer chromatographic examination.

In the Table
+ indicates that no decomposition of the active substance was visible (less than 10 % decomposed)
- indicates that a distinct decomposition of the active substance was visible.

TABLE I

Stabilizer	after 7 days	after 14 days	after 40 days
none	—	—	—
oxalic acid	+	+	+
malonic acid	+	+	+
maleic acid	+	+	+
glycollic acid	+	+	+
lactic acid	+	+	+
citric acid	+	+	+
phthalic acid	+	+	+
5-nitro-isophthalic acid	+	+	+
2-nitro-benzoic acid	+	+	+
3,5-dinitrobenzoic acid	+	+	+
4-chloro-3-nitro-benzoic acid	+	+	+
2-chloro-3,5-dinitrobenzoic acid	+	+	+
methanesulphonic acid	+	+	+
benzenesulphonic acid	+	+	+
para-toluenesulphonic acid	+	+	+
tetrapropylene-benzenesulphonic acid	+	+	+
Stabilizers according to U.S. Specifications No. 2,954,396			
phosphoric acid	+	—	—
acetic acid	—	—	—

	Similar results were also obtained, for example, with the following compounds:	indicated in Table II below was added to a liquid preparation having the following composition:	30
	(3 - methoxycarbonylamino - phenyl) - N-phenyl carbamate,		
5	(3 - ethoxycarbonylamino - phenyl) - N - (3-methyl - phenyl) - carbamate,	16.4 % by weight of (3 - methoxycarbonylamino - phenyl) - N-	
	(3 - ethoxycarbonylamino - phenyl) - N-(phenyl - carbamate,	(3 - methyl - phenyl)-	35
	(3 - methoxycarbonylamino - phenyl) - N - (3-chloro - phenyl) - carbamate,	emulsifier (a mixture	
10	(3 - ethoxycarbonylamino - phenyl) - N - (3-chloro - phenyl) - carbamate,	of an alkylbenzene-	
	(3 - methoxycarbonylamino - phenyl) - N-	sulphonate, a poly-	
	(n - butyl) - carbamate,	ethoxylated fatty acid	40
15	(3 - Methoxycarbonylamino - phenyl) - N-(tertiary butyl) - carbamate,	and a polyethoxylated	
	(3 - methoxycarbonylamino - phenyl) - N-	alkylphenol)	
	(secondary butyl) - carbamate,	3.6 % " " " a mixture of high-	
	(3 - methoxycarbonylamino - phenyl) - N-	boiling aromatic	
	(3 - methoxycarbonylamino - phenyl) - N-	hydrocarbons and	45
20	[pentyl - (2)] - carbamate,	60.0 % " " " isophorone	
	(3 - methoxycarbonylamino - phenyl) - N-		
	(neopentyl) - carbamate and		
	(3 - methoxycarbonylamino - phenyl) - N-		
	(3,5 - dimethyl - phenyl) - carbamate.		

25

Example 2

A series of experiments were carried out in which an increasing quantity of the stabilizer

and the resulting preparations were stored at the temperatures indicated in the following Table. After the periods of time shown in the Table samples were taken and the degree of decomposition of the active substance was determined quantitatively and expressed as a percentage.

50

TABLE II

Stabilizer as a % by weight	temp. °C.	after 14 days	after 28 days	after 40 days	after 90 days
none	20	—	—	5%	10%
	50	20%	35%	45%	70%
	70	75%	90%	100%	100%
0.25% citric acid	20	0%	0%	—	—
	70	0%	0%	—	—
0.5% citric acid	20	0%	0%	0%	—
	70	0%	0%	0%	—
1.0% citric acid	20	0%	0%	0%	—
	70	0%	0%	0%	—
0.5% malonic acid	20	0%	0%	0%	—
	70	0%	0%	<5%	—
1.0% malonic acid	20	0%	0%	0%	0%
	70	0%	0%	0%	<10%
0.5% 3,5-dinitrobenzoic acid	20	0%	0%	0%	—
	70	0%	0%	<5%	—
1.0% 3,5-dinitrobenzoic acid	20	0%	0%	0%	—
	70	0%	0%	0%	—

Example 3

A series of experiments were carried out in which the stabilizers indicated in Table III below were added in the amounts given to a liquid preparation having the following composition:

- 16.7 % by weight of (3 - ethoxycarbonyl-amino - phenyl) - N-(3 - methyl - phenyl)-carbamate
- 20.9 % " " " emulsifier (a mixture of an alkylbenzene-sulphonate, a polyethoxylated fatty acid and a polyethoxylated alkylphenol)
- 4.2 % " " " a mixture of high-boiling aromatic hydrocarbons

4.2 % " " " methylhexalin and
54.0 % " " " isophorone

and the resulting preparations were stored at 55 and 70°C respectively. After the indicated periods of time samples were taken and subjected to a thin-layer chromatographic examination.

In the Table

- + indicates that no decomposition of the substance was visible
- (+) indicates that a slight decomposition of the active substance was visible
- indicates that a considerable decomposition of the active substance was visible

TABLE III

Stabilizer as a % by weight	temperature °C	after 7 days	after 14 days	after 40 days
none	55	(+)	(+)	—
	70	(+)	—	—
1% malonic acid	55	+	+	+
	70	+	+	(+)
1% maleic acid	55	+	+	+
	70	+	+	+

Example 4

5 A series of experiments were carried out in which the stabilizers indicated in Table IV below were added in the amounts given to a liquid preparation having the following composition:

10 16.7 % by weight of (3 - ethoxycarbonyl-
amino - phenyl) - N-
phenyl - carbamate
31.7 % " " " emulsifier (a mixture
of an alkylbenzene-
sulphonate, a poly-
15 ethoxylated fatty acid
and a polyethoxylated
alkylphenol)
33.3 % " " " isophorone
4.2 % " " " dibutylphthalate

1.6 % " " " methylhexalin and
12.5 % " " " tetralin

20

and the resulting preparations were stored at 55 and 70°C respectively. After the indicated periods of time samples were taken and subjected to a thin-layer chromatographic examination.

25

In the Table

+ indicates that no decomposition of the active substance was visible
(+) indicates that a slight decomposition of the active substance was visible
— indicates that a considerable decomposition of the active substance was visible

30

TABLE IV

Stabilizer as a % by weight	temperature °C	after 7 days	after 14 days	after 40 days
none	55	(+)	—	—
	70	(+)	—	—
1% malonic acid	55	+	+	+
	70	+	+	(+)
1% lactic acid	55	+	+	+
	70	+	+	+

Example 5

A series of experiments were carried out in which an increasing quantity of malonic acid was added to a liquid preparation having the following compositions:

- 5 12.5 % by weight of (3 - methoxycarbonyl-amino - phenyl) - N-(3 - methyl - phenyl)-carbamate
- 10 15.8 % " " " " emulsifier (a mixture of an alkylbenzene-sulphonate), a polyethoxylated fatty acid and a polyethoxylated alkylphenol)
- 15

3.3 % " " " " a mixture of high-boiling aromatic hydrocarbons and isophorone

and the resulting preparations were stored at 20°, 55° and 70°C respectively. After the periods of time shown in Table V below samples were taken and subjected to a thin-layer chromatographic examinations. In the Table

- + indicates that no decomposition of the active substance was visible
- (+) indicates that a slight decomposition of the active substance was visible
- indicates that a considerable decomposition of the active substance was visible.

TABLE V

Stabilizer as a % by weight	temperature °C.	after 7 days	after 14 days	after 40 days
none	20	+	+	(+)
	55	-	-	-
	70	-	-	-
0.1% malonic acid	20	+	+	+
	55	+	+	+
	70	+	+	(+)
0.25% malonic acid	20	+	+	+
	55	+	+	+
	70	+	+	+
0.5% malonic acid	20	+	+	+
	55	+	+	+
	70	+	+	+
1.0% malonic acid	20	+	+	+
	55	+	+	+
	70	+	+	+
2.0% malonic acid	20	+	+	+
	55	+	+	+
	70	+	+	+
5.0% malonic acid	20	+	+	+
	55	+	+	+
	70	+	+	+

Example 6

Experiments were carried out in which the amounts of stabilizer (namely malonic acid) indicated in Table VI below were added to a liquid preparation having the following compositions:

5	16.7 %	by weight of	(3 - methoxycarbonyl-phenyl) - N - phenyl-carbamate
10	20.4 %	" " "	emulsifier (a mixture of an alkylbenzene-sulphonate, a polyethoxylated fatty acid and a polyethoxylated alkylphenol)
15	58.3 %	" " "	isophorone and
	4.6 %	" " "	dimethylsulphoxide

and the resulting preparation was stored at 55° and 70°C respectively. For the purpose of comparison, the experiments were repeated with preparations having the composition indicated above but not containing a stabilizer. After the indicated periods of time samples were taken and subjected to a thin-layer chromatographic examination. In the Table

+ indicates that no decomposition of the active substance was visible
 (+) indicates that a slight decomposition of the active substance was visible
 - indicates that a considerable decomposition of the active substance was visible

TABLE VI

Stabilizer	temp. °C.	after 7 days	after 14 days	after 40 days
none	55	(+)	(+)	-
	70	(+)	-	-
1% by weight of malonic acid	55	+	+	+
	70	+	+	(+)

Example 7

1% by weight of malonic acid as stabilizer was added to a liquid preparation having the following composition:

35	12.5 %	by weight of	(3 - methoxycarbonyl-amino - phenyl) - N - (3 - methyl - phenyl)-carbamate
40	15.8 %	" " "	emulsifier (a mixture of an alkylbenzene-sulphonate, a polyethoxylated fatty acid and a polyethoxylated alkylphenol)
45	3.3 %	" " "	a mixture of high-boiling aromatic hydrocarbons and

68.4 % " " " cyclohexanone

and the resulting preparation was stored at 70°C. For the purpose of comparison, a preparation having the composition indicated above but not containing the stabilizer was also stored at 70°C. After the periods of time indicated in Table VII below samples were taken and subjected to a thin-layer chromatographic examination. In the Table

+ indicates that no decomposition of the active substance was visible
 - indicates that a considerable decomposition of the active substance was visible

TABLE VII

Stabilizer	after 26 days	after 40 days
none	-	-
1.0% by weight of malonic acid	+	+

Example 8

A series of experiments were carried out in which an increasing proportion of solvent was replaced by citric acid as stabilizer in an emulsion concentrate having the following composition:

- 5 3.6 % " " " " " " " "
- 10 16.4 % by weight of (3 - methoxycarbonyl-amino - phenyl) - N-(3 - methyl - phenyl)-carbamate
- 20.0 % " " " " " " " "
- emulsifier (a mixture of alkylbenzene - sul-

phonate, polyethoxylated castor oil and a polyethoxylated alkyl-phenol)

a mixture of high-boiling aromatic hydrocarbons and isophorone

15

20

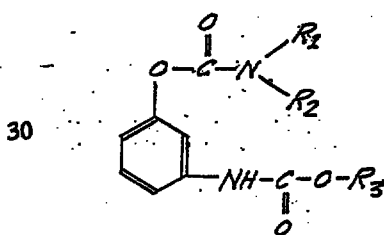
The resulting preparations were stored for 4 months at 70°C and then examined quantitatively to determine the degree of decomposition of the active substance.

TABLE VIII

Content as a % by weight of citric acid in the emulsion concentrate	Degree as a % of the decomposition of the active substance after 4 months' storage at 70°C.
0.00%	100%
0.05%	0%
0.10%	0%
0.25%	0%
0.50%	0%
1.00%	0%
5.00%	0%

WHAT WE CLAIM IS:—

1. A liquid herbicidal preparation which comprises a biscarbamate of the general formula I



in which R₁ represents an alkyl group, a cyclo-alkyl group, an unsubstituted aryl group or an aryl group substituted by one or more substituents selected from halogen atoms, alkyl groups and trifluoromethyl groups, R₂ represents a hydrogen atom and R₃ represents an unsubstituted or a terminally halogeno-substituted alkyl, alkenyl or alkynyl group, an organic solvent, a surface-active agent and a stabilizer selected from aliphatic dicarboxylic acids, aliphatic hydroxycarboxylic acids, nitro-substituted aromatic monocarboxylic acids,

aromatic dicarboxylic acids, aliphatic sul-phonic acids and aromatic sulphonic acids.

2. A liquid herbicidal preparation as claimed in claim 1, wherein the preparation contains a single stabilizer as defined in claim 1.

3. A liquid herbicidal preparation as claimed in claim 2, wherein the stabilizer is present in a concentration within the range of from 0.5 to 5 % by weight.

4. A liquid herbicidal preparation as claimed in claim 3, wherein the stabilizer is present in a concentration within the range of from 0.25 to 1.0 % by weight.

5. A liquid herbicidal preparation as claimed in claim 1, wherein the preparation contains two or more stabilizers as defined in claim 1.

6. A liquid herbicidal preparation as claimed in claim 5, wherein the stabilizers are present in a total concentration within the range of from 0.05 to 5 % by weight.

7. A liquid herbicidal preparation as claimed in claim 6, wherein the stabilizers are present in a total concentration within the range of from 0.25 to 1.0 % by weight.

8. A liquid herbicidal preparation as

45

50

55

60

65



Example 8

A series of experiments were carried out in which an increasing proportion of solvent was replaced by citric acid as stabilizer in an emulsion concentrate having the following composition:

16.4 % by weight of (3 - methoxycarbonyl-amino - phenyl) - N-(3 - methyl - phenyl)-carbamate
20.0 % " " " emulsifier (a mixture of alkylbenzene - sul-

phonate, polyethoxylated castor oil and a polyethoxylated alkyl-phenol)
a mixture of high-boiling aromatic hydrocarbons and isophorone

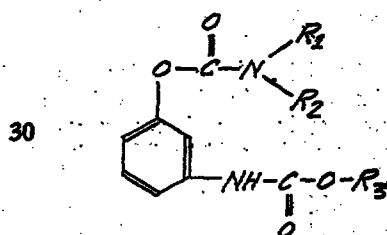
The resulting preparations were stored for 4 months at 70°C and then examined quantitatively to determine the degree of decomposition of the active substance.

TABLE VIII

Content as a % by weight of citric acid in the emulsion concentrate	Degree as a % of the decomposition of the active substance after 4 months' storage at 70°C.
0.00%	100%
0.05%	0%
0.10%	0%
0.25%	0%
0.50%	0%
1.00%	0%
5.00%	0%

WHAT WE CLAIM IS:—

1. A liquid herbicidal preparation which comprises a biscarbamate of the general formula I



in which R₁ represents an alkyl group, a cyclo-alkyl group, an unsubstituted aryl group or an aryl group substituted by one or more substituents selected from halogen atoms, alkyl groups and trifluoromethyl groups, R₂ represents a hydrogen atom and R₃ represents an unsubstituted or a terminally halogeno-substituted alkyl, alkenyl or alkynyl group, an organic solvent, a surface-active agent and a stabilizer selected from aliphatic dicarboxylic acids, aliphatic hydroxycarboxylic acids, nitro-substituted aromatic monocarboxylic acids,

aromatic dicarboxylic acids, aliphatic sul-phonic acids and aromatic sulphonic acids.

2. A liquid herbicidal preparation as claimed in claim 1, wherein the preparation contains a single stabilizer as defined in claim 1.

3. A liquid herbicidal preparation as claimed in claim 2, wherein the stabilizer is present in a concentration within the range of from 0.5 to 5 % by weight.

4. A liquid herbicidal preparation as claimed in claim 3, wherein the stabilizer is present in a concentration within the range of from 0.25 to 1.0 % by weight.

5. A liquid herbicidal preparation as claimed in claim 1, wherein the preparation contains two or more stabilizers as defined in claim 1.

6. A liquid herbicidal preparation as claimed in claim 5, wherein the stabilizers are present in a total concentration within the range of from 0.05 to 5 % by weight.

7. A liquid herbicidal preparation as claimed in claim 6, wherein the stabilizers are present in a total concentration within the range of from 0.25 to 1.0 % by weight.

8. A liquid herbicidal preparation as



* C L M S *

16

1,300,094

10

- claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is an aliphatic dicarboxylic acid.
9. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is oxalic acid.
10. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is malonic acid.
11. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is maleic acid.
12. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is an aliphatic hydroxycarboxylic acid.
13. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is glycollic acid.
14. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is lactic acid.
15. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is citric acid.
16. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is an aromatic dicarboxylic acid.
17. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is phthalic acid.
18. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is 5-nitroisophthalic acid.
19. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is a nitro-substituted aromatic monocarboxylic acid.
20. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is 2-nitrobenzoic acid.
21. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is 3,5-dinitrobenzoic acid.
22. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is 4-chloro-3-nitrobenzoic acid.
23. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is 2-chloro-3,5-dinitrobenzoic acid.
24. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is an aliphatic sulphonic acid.
25. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is methanesulphonic acid.
26. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is an aromatic sulphonic acid.
27. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is benzenesulphonic acid.
28. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is paratoluenesulphonic acid.
29. A liquid herbicidal preparation as claimed in any one of claims 2 to 7, wherein the stabilizer or one of the stabilizers is tetrapropylene-benzenesulphonic acid.
30. A liquid herbicidal preparation as claimed in any one of claims 2 to 29, wherein the preparation contains a single biscarbamate as defined in claim 1.
31. A liquid herbicidal preparation as claimed in claim 30, wherein the biscarbamate is present in a concentration within the range of from 5 to 50 % by weight.
32. A liquid herbicidal preparation as claimed in claim 31, wherein the biscarbamate is present in a concentration within the range of from 10 to 25 % by weight.
33. A liquid herbicidal preparation as claimed in any one of claims 2 to 29, wherein the preparation contains two or more biscarbamates as defined in claim 1.
34. A liquid herbicidal preparation as claimed in claim 33, wherein the biscarbamates are present in a total concentration within the range of from 5 to 50 % by weight.
35. A liquid herbicidal preparation as claimed in claim 34, wherein the biscarbamates are present in a total concentration within the range of from 10 to 25 % by weight.
36. A liquid herbicidal preparation as claimed in any one of claims 30 to 35, wherein the biscarbamate or one of the biscarbamates is (3 - methoxycarbonylamino - phenyl) - N-(3 - methyl - phenyl) - carbamate.
37. A liquid herbicidal preparation as claimed in any one of claims 2 to 36, wherein the preparation contains a single organic solvent.
38. A liquid herbicidal preparation as claimed in claim 37, wherein the organic solvent is present in a concentration within the range of from 10 to 90 % by weight.
39. A liquid herbicidal preparation as claimed in claim 38, wherein the organic solvent is present in a concentration within the

range of from 50 to 80 % by weight.

40. A liquid herbicidal preparation as claimed in any one of claims 2 to 36, wherein the preparations contains two or more organic solvents.

41. A liquid herbicidal preparation as claimed in claim 40, wherein the organic solvents are present in a total concentration within the range of from 10 to 90 % by weight.

42. A liquid herbicidal preparation as claimed in claim 41, wherein the organic solvents are present in a total concentration within the range of from 50 to 80 % by weight.

43. A liquid herbicidal preparation as claimed in any one of claims 2 to 42, wherein the preparation contains a single surface-active agent.

44. A liquid herbicidal preparation as claimed in claim 43, wherein the surface-active agent is present in a concentration within the range of from 2 to 40 % by weight.

45. A liquid herbicidal preparation as claimed in claim 44, wherein the surface-active agent is present in a concentration within the range of from 10 to 25 % by weight.

46. A liquid herbicidal preparation as claimed in any one of claims 2 to 42, wherein the preparation contains two or more surface-active agents.

47. A liquid herbicidal preparation as claimed in claim 46, wherein the surface-active agents are present in a total concentration within the range of from 2 to 40 % by weight.

48. A liquid herbicidal preparation as claimed in claim 47, wherein the surface-active agents are present in a total concentration within the range of from 10 to 25 % by weight.

49. Any one of the liquid herbicidal preparations as claimed in claim 1 and substantially as described in Examples 1 to 7 herein.

50. Any one of the liquid herbicidal preparations as claimed in claim 1 and substantially as described in Example 8 herein.

51. A method of selectively controlling weeds in a crop area, wherein a crop area is

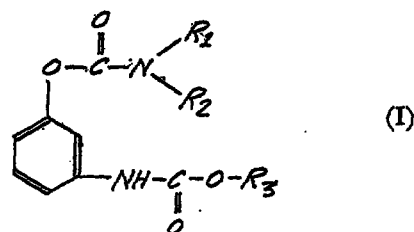
treated with a liquid herbicidal preparation as claimed in claim 1.

52. A method of selectively controlling weeds in a crop area, wherein a crop area is treated with a liquid herbicidal preparation as claimed in any one of claims 2 to 48.

53. A method of selectively controlling weeds in a crop area, wherein a crop area is treated with a liquid herbicidal preparation as claimed in claim 49.

54. A method of selectively controlling weeds in a crop area, wherein a crop area is treated with a liquid herbicidal preparation as claimed in claim 50.

55. A preparation which comprises a bis-carbamate of the general formula I



in which R_1 represents an alkyl group, a cycloalkyl group, an unsubstituted aryl group or an aryl group substituted by one or more substituents selected from halogen atoms, alkyl groups and trifluoromethyl groups, R_2 represents a hydrogen atom and R_3 represents an unsubstituted or a terminally halogeno-substituted alkyl, alkenyl or alkynyl group, and a stabilizer selected from aliphatic dicarboxylic acids, aliphatic hydroxycarboxylic acids, nitro-substituted aromatic monocarboxylic acids, aromatic dicarboxylic acids, adipic sulphonic acids and aromatic sulphonic acids.

56. A preparation as claimed in claim 55, wherein the preparation also contains a surface-active agent.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303-306, High Holborn,
London, W.C.1.