

L127050



PATENT SPECIFICATION

NO DRAWINGS

L127050

Date of Application and filing Complete Specification: 1 April, 1966.
No. 14543/66.

Application made in Germany (No. Sch36854 IVb/12a) on 9 April, 1965.

Complete Specification Published: 11 Sept., 1968.

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Index at acceptance:—C2 C(1F1B, 1F1C5, 1F1D2, 1Q6B1, 1Q6B2, 1Q7A, 1Q8A, 1Q8C, 1Q9A, 1Q11G, 1Q11J, 2B40C, 2B40D, 2B40G, 2B40J1, 2B40J3, 2B40L2); A5 E(1C4A2, 1C4A3, 1C4A4, 1C4B2, 1C4B3, 1C4B4)

Int. Cl.:—C 07 c 125/06

COMPLETE SPECIFICATION

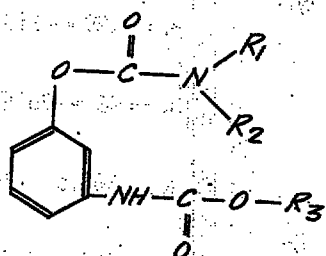
Substituted Phenylcarbamates and Herbicidal preparations thereof

We, SCHERING AKTIENGESELLSCHAFT, a body corporate organised according to the laws of Germany, of 170—172 Mullerstrasse, Berlin N.65, 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:—

This invention is concerned with new substituted phenylcarbamates and herbicidal preparations thereof.

The herbicidal action of phenylcarbamates, for example, isopropyl N-phenylcarbamate and isopropyl N-(3-chlorophenyl)-carbamate, is known. However, these substances have an insufficiently broad spectrum, since they have either no effect or only an inadequate effect on important weeds such as groundsel, wild camomile, galinsoga, and others.

The observation has been made that preparations containing at least one compound of the general formula



in which R₁ represents an alkyl group, a cycloalkyl group or an aryl group, which last may be substituted by a halogen atom and/or an alkyl group and/or a trifluoromethyl group, R₂ represents a hydrogen atom or an alkyl group, or R₁ and R₂ together with the nitrogen atom may form a heterocyclic ring that may contain further nitrogen and/or oxygen atoms and R₃ represents an alkyl, alkenyl or alkynyl group that may be substituted by a terminal halogen atom, together with a solid or liquid carrier or diluent material, are effective against a very wide variety of weeds, including, in particular, dicotyledons.

The herbicidal action is to be observed in both pre-emergence and post-emergence treatments, which thus allows preparations containing the said compounds to be applied by whichever method is desired. The herbicidal action is also to be observed when they are applied to the leaves of established weeds (contact treatment), which is a further advantage.

It has also been observed that a few of the compounds, notably methyl N-(3-[N'-(3'-methylphenyl)-carbamoyloxy]-phenyl)-carbamate and ethyl N-(3-(N'-phenyl-carbamoyloxy)-phenyl)-carbamate, have a selective herbicidal action and can be used, for example, to combat weeds in beet fields.

The invention accordingly also provides a process for selectively combatting weeds in a crop area, wherein there is used a preparation as specified including a compound of the above general formula.

Examples of compounds that can be used in accordance with the invention are as follows:—

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Compound No.	Name of compound	Physical constants
1	ethyl N-(3-(N'-(2'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 117 — 119°C.
2	β -chlorethyl N-(3-(N'-(2'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 116 — 117°C.
3	methyl N-(3-(N'-(3'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 153 — 155°C.
4	ethyl N-(3-(N'-(3'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 127 — 128°C.
5	methyl N-(3-(N'-(4'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 178°C.
6	ethyl N-(3-(N'-(4'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 150 — 151°C.
7	n-propyl N-(3-(N'-(4'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 147°C.
8	n-butyl N-(3-(N'-(4'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 138°C.
9	methyl N-(3-(N'-(2'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 158 — 160°C.
10	ethyl N-(3-(N'-(2'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 126 — 127°C.
11	β -chlorethyl N-(3-(N'-(2'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 129 — 130°C.
12	butyn-(1)-yl-(3) N-(3'-(N'-(3''-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 140 — 141°C.
13	butyn-(1)-yl-(3) N-(3'-(N'-(4''-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 153 — 155°C.
14	butyn-(1)-yl-(3) N-(3'-(N'-(3''-trifluoromethylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 129 — 130°C.
15	ethyl N-(3-(N',N'-diethylcarbamoyloxy)-phenyl)-carbamate	m.p. = 75 — 76°C.
16	ethyl N-(3-(N',N'-pentamethylene-carbamoyloxy)-phenyl)-carbamate	m.p. = 103.5 — 105.5°C.
17	ethyl N-(3-(N'-methylcarbamoyloxy)-phenyl)-carbamate	m.p. = 131 — 132°C.
18	β -chlorethyl N-(3-(N'-methylcarbamoyloxy)-phenyl)-carbamate	m.p. = 127 — 128°C.
19	n-propyl N-(3-(N'-methylcarbamoyloxy)-phenyl)-carbamate	m.p. = 125 — 127°C.
20	n-butyl N-(3-(N'-methylcarbamoyloxy)-phenyl)-carbamate	m.p. = 111 — 112°C.

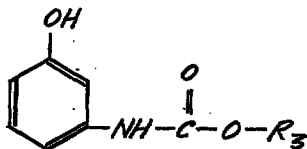
Compound No.	Name of compound	Physical constants
21	methyl N-(3-(N'-n-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 114 — 115°C.
22	ethyl N-(3-(N'-n-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 99.5°C.
23	sec.-butyl N-(3-(N'-n-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 142 — 143°C.
24	methyl N-(3-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 159 — 161°C.
25	ethyl N-(3-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 128°C.
26	β -chlorethyl N-(3-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 147 — 148°C.
27	n-propyl N-(3-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 160°C.
28	n-butyl N-(3-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 140 — 141°C.
29	ethyl N-(3-(N'-(3'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 128 — 129°C.
30	β -chlorethyl N-(3-(N'-(3'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 118 — 119°C.
31	methyl N-(3-(N'-(4'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 162 — 163.5°C.
32	ethyl N-(3-(N'-(4'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 147 — 148°C.
33	ethyl N-(3-(N'-(3'-trifluoromethylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 130 — 131°C.
34	β -chlorethyl N-(3-(N'-(3'-trifluoromethylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 132 — 133°C.
35	butyn-(1)-yl-(3) N-(3'-(N'-methylcarbamoyloxy)-phenyl)-carbamate	m.p. = 157 — 159°C.
36	butyn-(1)-yl-(3) N-(3'-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 146 — 147°C.
37	butyn-(1)-yl-(3) N-(3'-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 164 — 166°C.
38	butyn-(1)-yl-(3) N-(3'-(N'-(2"-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 134 — 136°C.
39	butyn-(1)-yl-(3) N-(3'-(N'-(4"-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 153 — 155°C.
40	butyn-(1)-yl-(3) N-(3'-(N'-(2"-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 155 — 156°C.

Compound No.	Name of compound	Physical constants
41	sec.-butyl N-(3-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 149 — 150°C.
42	methyl N-(3-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 152°C.
43	ethyl N-(3-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 118 — 119°C.
44	β -chloroethyl N-(3-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 149 — 150°C.
45	n-propyl N-(3-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 125 — 126°C.
46	isopropyl N-(3-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 133 — 135°C.
47	n-butyl N-(3-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 145°C.
48	sec.-butyl N-(3-(N'-phenylcarbamoyloxy)-phenyl)-carbamate	m.p. = 145 — 147°C.
49	methyl N-(3-(N'-(2'-chlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 124 — 126°C.
50	methyl N-(3-(N'-(3'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 139 — 142°C.
51	morpholine-N-carboxylic acid 3-carbethoxy-aminophenyl ester	m.p. = 114 — 115°C.
52	ethyl N-(3-(N'-(α -naphthyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 150 — 151°C.
53	methyl N-(3-(N'-(α -naphthyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 166 — 168°C.
54	ethyl N-(3-(N'-(3',4'-dichlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 154 — 155°C.
55	methyl N-(3-(N'-methylcarbamoyloxy)-phenyl)-carbamate	m.p. = 126 — 127°C.
56	methyl N-(3-(N'-(3',4'-dichlorophenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 188 — 190°C.
57	methyl N-(3-(N'-(3'-chloro-4'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 167 — 168°C.
58	ethyl N-(3-(N'-(3'-chloro-4'-methylphenyl)-carbamoyloxy)-phenyl)-carbamate	m.p. = 150 — 151°C.
59	n-propyl N-(3-(N'-ethylcarbamoyloxy)-phenyl)-carbamate	m.p. = 120°C.
60	n-propyl N-(3-(N'-n-propylcarbamoyloxy)-phenyl)-carbamate	m.p. = 122°C.

Compound No.	Name of compound	Physical constants
61	n-propyl N-(3-(N'-isopropylcarbamoyloxy)-phenyl)-carbamate	m.p. = 154°C.
62	n-propyl N-(3-(N'-n-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 117°C.
63	n-butyl N-(3-(N'-ethylcarbamoyloxy)-phenyl)-carbamate	m.p. = 112°C.
64	n-butyl N-(3-(N'-isopropylcarbamoyloxy)-phenyl)-carbamate	m.p. = 129°C.
65	n-butyl N-(3-(N'-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 108°C.
66	isopropyl N-(3-(N'-ethylcarbamoyloxy)-phenyl)-carbamate	m.p. = 145.5—147°C.
67	isopropyl N-(3-(N'-isopropylcarbamoyloxy)-phenyl)-carbamate	m.p. = 155.5 — 158°C.
68	isopropyl N-(3-(N'-n-propylcarbamoyloxy)-phenyl)-carbamate	m.p. = 142 — 144°C.
69	isopropyl N-(3-(N'-n-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 143 — 144°C.
70	isopropyl N-(3-(N'-cyclohexylcarbamoyloxy)-phenyl)-carbamate	m.p. = 157.5 — 158.5°C.
71	methyl N-(3-(N'-ethylcarbamoyloxy)-phenyl)-carbamate	m.p. = 148 — 151°C.
72	methyl N-(3-(N'-isopropylcarbamoyloxy)-phenyl)-carbamate	m.p. = 156 — 159.5°C.
73	methyl N-(3-(N'-n-propylcarbamoyloxy)-phenyl)-carbamate	m.p. = 142 — 144°C.
74	ethyl N-(3-(N'-ethylcarbamoyloxy)-phenyl)-carbamate	m.p. = 146.5 — 149°C.
75	ethyl N-(3-(N'-isopropylcarbamoyloxy)-phenyl)-carbamate	m.p. = 163 — 166°C.
76	ethyl N-(3-(N'-n-propylcarbamoyloxy)-phenyl)-carbamate	m.p. = 134 — 137°C.
77	n-propyl N-(3-(N'-tert.-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 164 — 165°C.
78	ethyl N-(3-(N'-tert.-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 159 — 160°C.
79	methyl N-(3-(N'-tert.-butylcarbamoyloxy)-phenyl)-carbamate	m.p. = 165 — 166°C.
80	isopropyl N-(3-(N'-methylcarbamoyloxy)-phenyl)-carbamate	m.p. = 155.5 — 157°C.

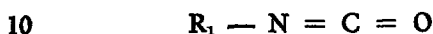
The hitherto unknown compounds can be prepared, for example, by the following processes:—

- 5 When R_2 represents a hydrogen atom, by reacting N-hydroxyphenylurethanes of the general formula



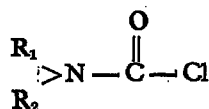
with

- a) isocyanates of the general formula



in the presence of a catalyst, advantageously an organic base, preferably triethylamine, or with

- 15 b) carbamic acid chlorides of the general formula



- 20 in the presence of an acid acceptor, advantageously an inorganic or organic base, preferably pyridine, or, when R_2 represents alkyl, or is a member of a heterocyclic ring, the indicated N-hydroxyphenylurethanes are reacted as indicated with the indicated carbamic acid chlorides, R_1 and R_2 in the above formulae having the meanings given above and R_2 having the corresponding meaning in each case.

The following Examples 1 and 2 illustrate the preparation of the new phenylcarbamates.

30 EXAMPLE 1

Methyl N - (3 - (N' - phenylcarbamoyloxy) - phenyl) - carbamate

- 35 16.7 Grams (0.1 mol) of methyl N - (3 - hydroxyphenyl) - carbamate are dissolved in 50 ml of tetrahydrofuran. 0.5 Millilitre of triethylamine is added to the solution and this is followed by 12 ml (0.11 mol) of phenylisocyanate. The batch is allowed to stand for 20 hours at room temperature, light petroleum is added and the carbamate crystallizes.

Yield: 27.5 grams (96% of the theoretical yield).

M.p. 152°C.

Analysis for $C_{16}H_{14}N_2O_4$

45 Calculated:

C = 62.90% H = 4.93% N = 9.78%

Found:

C = 62.6% H = 5.00% N = 9.69%

EXAMPLE 2

Ethyl N - (3 - (N',N' - pentamethylene - carbamoyloxy) - phenyl) - carbamate

14.5 Grams (0.08 mol) of ethyl N - (3 - hydroxyphenyl) - carbamate are dissolved in 30 ml of anhydrous pyridine and then 13.1 grams (0.088 mol) of piperidine-N-carboxylic acid chloride are added to the solution. After 2 hours at room temperature, the batch is heated for 90 minutes on a steam bath. Subsequently, the pyridine is evaporated *in vacuo* and the residue is dissolved in ether and dilute sodium hydroxide solution in the presence of ice. The solution in ether is washed successively with water, dilute hydrochloric acid, water and dilute $KHCO_3$ solution, the temperature being kept at 0°C by the addition of ice. After drying with sodium sulphate and evaporating a large proportion of the ether, petroleum ether is added and the carbamate crystallizes.

Yield: 15.8 grams (68% of the theoretical yield)

M.p. 103.5 to 105.5°C.

Analysis for $C_{15}H_{20}N_2O_4$

Calculated:

C = 61.65% H = 6.90% N = 9.59%

Found:

C = 61.18% H = 7.00% N = 9.56%

The new phenylcarbamates are very sparingly soluble or insoluble in water, benzene and petroleum and moderately to readily soluble in acetone, isophorone, dimethylformamide and dimethylsulphoxide.

The N-hydroxyphenylurethanes required as starting products in their manufacture, some of which have not yet been described in the literature, may be prepared in known manner, for example, by N-acylation of meta-aminophenol with the appropriate chloroformic acid esters, for example, in a mixture of ethyl acetate and water in the presence of magnesium oxide.

The preparation of one of the starting products is described in the following:—

21.8 Grams (0.2 mol) of meta-aminophenol and 5 grams of magnesium oxide are taken up in 70 ml of water and 70 ml of ethyl acetate. 26.5 Grams (0.2 mol) of chloroformic acid butyn - (1) - yl - (3) - ester are added dropwise while stirring, the batch being cooled to 10 to 15°C, and stirring is then continued for 30 minutes at room temperature; subsequently, the excess magnesium oxide is dissolved in dilute hydrochloric acid, and the organic phase is washed neutral with a small amount of water and then with dilute potassium bicarbonate solution. After drying with sodium sulphate and evaporation of the ethyl acetate *in vacuo*, the crude product is purified by dissolving it in a small amount of ether, filtering the solution and crystallizing out the butyn - (1) - yl -

(3) N - (3 - hydroxyphenyl) - carbamate by the addition of light petroleum.

C = 64.38% H = 5.40% N = 6.83%

Found:

C = 64.23% H = 5.59% N = 6.90%

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Yield: 34 grams (83% of the theoretical yield)

M.p. 94 to 95°C.

Analysis for $C_{11}H_{11}NO_3$

Calculated:

The other N-hydroxyphenylurethanes needed as starting products can be prepared in the same manner; some of them are listed in the following table:—

methyl N-(3-hydroxyphenyl)-carbamate	m.p. = 94 — 95°C.
ethyl N-(3-hydroxyphenyl)-carbamate	m.p. = 94 — 95°C.
n-propyl N-(3-hydroxyphenyl)-carbamate	m.p. = 71 — 73°C.
isopropyl N-(3-hydroxyphenyl)-carbamate	m.p. = 75 — 76°C.
n-butyl N-(3-hydroxyphenyl)-carbamate	m.p. = 87 — 88°C.
sec.-butyl N-(3-hydroxyphenyl)-carbamate	m.p. = 115 — 116.5°C.
β-chlorethyl N-(3-hydroxyphenyl)-carbamate	m.p. = 87.5°C.

The new phenylcarbamates of the invention may be used either alone or in admixture with one another and/or other herbicides and/or other substances, for example, fertilizers, for combating weeds.

They are advantageously used in a form commonly used for combating weeds, for example as powders, strewing agents, granulates, solutions, emulsions or suspensions, in the presence of liquid and/or solid excipients or diluents and, if necessary, wetting agents, adhesives, emulsifiers and/or dispersing agents.

The preparations in their various forms are made by methods normally used for preparations for plant protection with the use of liquid or solid inert support substances or diluents and, if necessary, surface-active substances.

Suitable liquid excipients are, for example, organic solvents, for example, isophorone, decalin, tetralin, dimethylformamide and dimethylsulphoxide.

Suitable solid excipients are, for example,

chalk, kaolin, talcum, natural or synthetic silicic acid, Attaclay and other clays.

Suitable surface-active substances are, for example, salts of lignosulphonic acid, salts of alkylated benzenesulphonic acids, sulphonated acid amides and the salts thereof, polyglycols, polyethoxylated amines, alcohols and phenols.

Rates of application of the order of about 0.3 kg of active substance per hectare have been found to be adequate for the selective combating of weeds.

The herbicidal action of the preparations of the invention is illustrated by the following Examples:—

EXAMPLE 3

The compounds listed in the following table were sprayed on to mustard and tomato plants in a greenhouse at a rate of 10 kg of active substance per hectare, suspended in 800 litres of water per hectare. The test plants were destroyed, which was not the case with isopropyl N - phenyl - carbamate, which was used as control.

Compound No.	Mustard	Tomatoes
1	0	1
2	0	1
3	0	0
4	0	0
5	0	5
6	0	1

Compound No.	Mustard	Tomatoes
7	0	7
8	0	7
9	0	0
10	1	9
11	0	3
12	0	2
13	0	1
14	0	1
15	0	0
16	0	0
17	0	0
18	1	7
19	0	1
20	0	0
21	0	1
22	0	0
23	0	6
24	0	0
25	0	0
26	1	1
27	0	5
28	0	7
29	0	0
30	0	1
31	0	1
32	0	0
33	0	0
34	0	1
35	1	4
36	0	0
37	0	1

Compound No.	Mustard	Tomatoes
38	0	1
39	0	1
40	0	0
41	1	4
42	0	0
43	0	0
44	0	1
45	0	1
46	0	2
47	0	1
48	0	1
49	0	2
50	0	0
51	1	0
52	0	0
53	0	1
54	1	1
55	0	0
56	2	4
57	0	1
58	1	3
59	0	0
60	0	0
61	0	0
62	0	0
63	0	0
64	1	0
65	0	1
66	3	3
67	0	0
68	0	0

Compound No.	Mustard	Tomatoes
69	0	0
70	0	1
71	0	2
72	0	0
73	0	1
74	0	3
75	0	5
76	0	1
77	0	0
78	0	0
79	0	0
80	0	3
isopropyl N-phenyl carbamate	7	8

0 = completely destroyed

10 = no effect

EXAMPLE 4

5 The compounds listed in the following table were sprayed on to crop plants and weeds at a rate of 1 kg of active substance per hectare, suspended in 800 litres of water per hectare,

in a greenhouse. It can be seen from the results that isopropyl N - (3 - chlorophenyl) - carbamate has only a very slight effect compared with the compounds of the invention.

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Compound No.	Peas	Sugar beet	Carrots	Onions	Sinapis arvensis	Solanum ssp.	Varianella ssp.	Stellaria media	Galinsoga parviflora	Senecio vulgaris	Matricaria chamomilla
3	10	10	10	10	1	2	0	4	4	1	5
4	10	10	10	10	0	0	0	1	2	0	1
9	10	10	10	10	4	10	1	4	2	3	1
20	10	0	10	10	1	1	0	0	0	0	0
21	10	5	7	10	0	1	0	0	0	0	0
22	10	4	7	10	0	4	0	0	0	0	0
24	10	7	7	10	0	3	0	0	0	1	0
25	10	0	10	10	0	0	0	0	0	0	10
29	10	10	10	10	0	5	0	1	0	2	2
42	10	10	10	10	0	7	0	0	0	5	10
43	10	10	10	10	0	0	0	0	0	0	0
50	10	10	10	10	0	4	0	0	0	0	0
55	8	2	8	10	0	1	0	0	1	2	0
67	10	2	10	10	0	0	0	0	0	4	0
80	10	10	10	10	0	10	0	0	2	6	3
isopropyl N-(3-chlorophenyl)-carbamate	7	10	10	10	5	10	10	7	10	10	10

0 = completely destroyed
10 = no effect

EXAMPLE 5

The compounds listed in the following table were used in the pre-emergence treatment of crop plants and weeds, the said compounds being sprayed on to the sandy soil at a rate of 0.3 kg of active substance per hectare, suspended in 800 litres of water per hectare. The tests were carried out in a greenhouse. The

results clearly illustrate the greater efficacy of the preparations of the invention in combating subborn weeds such as galinsoga (*Galinsoga parviflora*), groundsel (*Senecio vulgaris*) and wild camomile (*Matricaria chamomilla*), which cannot be dealt with by isopropyl N - (3 - chlorophenyl) - carbamate.

Compound No.	Peas	Sugar beet	Carrots	Onions	Sinapis arvensis	Solanum ssp.	Varianella ssp.	Stellaria media	Galinsoga parviflora	Senecio vulgaris	Matricaria chamomilla
21	10	10	10	10	4	10	10	0	1	1	1
24	10	0	10	4	0	0	0	0	0	0	0
25	10	10	10	10	0	0	0	0	0	0	0
isopropyl N-(3-chlorophenyl)-carbamate	10	10	10	10	10	0	10	0	10	10	10

0 = completely destroyed

10 = no effect

EXAMPLE 6

The compounds listed in the following table were used in a field test in the form of aqueous emulsions or suspensions on crop plants and weeds at the 2-leaf and 4-leaf stage, the said compounds being sprayed on to the plants at a rate of 2 and 5 kg of active substance per hectare. The crop plants were sugar beet and peas and the weeds were the annual weeds

Sinapis ssp., *Papaver ssp.*, *Chenopodium album*, *Spergula arvensis*, *Centaurea ssp.*, *Senecio vulgaris*, *Galinsoga parviflora* and *Lamium amplexicaule*. As can be seen from the table, the control substance isopropyl N - (3 - chlorophenyl) - carbamate has only a very weak post-emergence effect without displaying any selectivity as compared with the preparations of the invention.

Compound No.	kg active substance/ha	Peas	Sugar beet	Sinapis ssp.	Papaver ssp.	Chenopodium album	Spergula arv.	Cnetaurea ssp.	Senecio vulg.	Galinoga parv.	Lamium amplexicaule
21	2 5	10 10	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
24	2 5	10 10	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
25	2 5	10 10	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
43	2 5	10 10	10 10	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
50	2 5	10 10	10 10	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
isopropyl (3-chlorophenyl)-carbamate	2 5	7 3	10 5	9 7	9 8	9 6	6 3	10 10	10 10	10 10	10 10

10 = not damaged

0 = completely destroyed

EXAMPLE 7

Preparation of an emulsion concentrate

A mixture was prepared from the following

5 ingredients:—

20% by weight of one of the new phenyl-carbamates
 15% by weight of an emulsifier based on polyglycol
 45% by weight of isophorone
 15% by weight of tetralin
 5% by weight of dimethylsulphoxide.

EXAMPLE 8

Preparation of a wettable powder

A mixture was prepared from the following

15 ingredients with the aid of an air-jet

blender:—

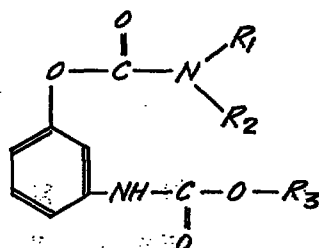
50% by weight of one of the new phenyl-carbamates
 15% by weight of calcium lignosulphonate
 35% by weight of talcum
 The preparations described in Examples 7 and 8 can be mixed with water and used in the form of aqueous emulsions or suspensions in the manner described above.

25



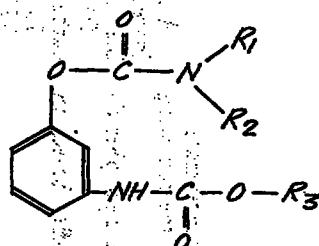
WHAT WE CLAIM IS:—

1. Herbicidal preparations which contain at least one compound of the general formula

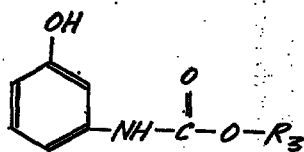


- 5 in which R_1 represents an alkyl group, a cyclo-alkyl group or an aryl group, which last may be substituted by a halogen atom and/or an alkyl group and/or a trifluoromethyl group, R_2 represents a hydrogen atom or an alkyl group, or R_1 and R_2 , together with the nitrogen atom, may form a heterocyclic ring that may contain further nitrogen and/or oxygen atoms and R_3 represents an alkyl, alkenyl or alkynyl group that may be substituted by a terminal halogen atom, together with a solid or liquid carrier or diluent material.

2. A process for the manufacture of phenyl-carbamates of the general formula

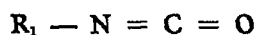


- 20 in which R_1 represents an alkyl group, a cyclo-alkyl group or an aryl group, which last may be substituted by a halogen atom and/or an alkyl group and/or a trifluoromethyl group, R_2 represents a hydrogen atom or an alkyl group, or R_1 and R_2 , together with the nitrogen atom, may form a heterocyclic ring that may contain further nitrogen and/or oxygen atoms and R_3 represents an alkyl, alkenyl or alkynyl group that may be substituted by a terminal halogen atom, wherein, when R_2 represents a hydrogen atom, N-hydroxyphenylurethanes of the general formula



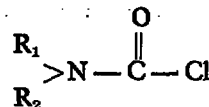
are reacted with

- 35 a) isocyanates of the general formula



in the presence of a catalyst, or with

b) carbamic acid chlorides of the general formula



40

in the presence of an acid acceptor, or, when R_2 represents alkyl or is a member of a heterocyclic ring, the indicated N-hydroxyphenylurethanes are reacted as indicated with the indicated carbamic acid chlorides, R_1 and R_2 in the formulae of the reactants having the meanings given above and R_3 having the corresponding meaning in each case.

3. A process as claimed in claim 2, wherein the catalyst in reaction a) is an organic base.

45

4. A process as claimed in claim 3, wherein the organic base is triethylamine.

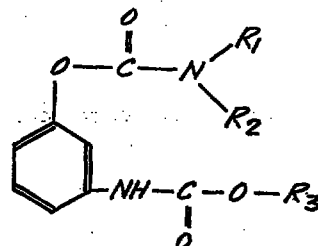
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5. A process as claimed in any one of claims 2—4, wherein the acid acceptor in reaction b) is an inorganic or organic base.

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6. A process as claimed in claim 5, wherein as organic base pyridine is used.

7. Compounds of the general formula



in which R_1 represents an alkyl group, a cyclo-alkyl group or an aryl group, which last may be substituted by a halogen atom and/or an alkyl group and/or a trifluoromethyl group, R_2 represents a hydrogen atom or an alkyl group, or R_1 and R_2 , together with the nitrogen atom, may form a heterocyclic ring that may contain further nitrogen and/or oxygen atoms and R_3 represents an alkyl, alkenyl or alkynyl group that may be substituted by a terminal halogen atom.

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8. Ethyl N - (3 - (N' - (2' - chlorophenyl) - carbamoyloxy) - phenyl) - carbamate.

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9. β - Chlorethyl N - (3 - (N' - (2' - chlorophenyl) - carbamoyloxy) - phenyl) - carbamate.

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10. Methyl N - (3 - (N' - (3' - chloro - phenyl) - carbamoyloxy) - phenyl) - carbamate.

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11. Ethyl N - (3 - (N' - (3' - chlorophenyl) - carbamoyloxy) - phenyl) - carbamate.

12. Methyl N - (3 - (N' - (4' - chloro - phenyl) - carbamoyloxy) - phenyl) - carbamate.

80

13. Ethyl N - (3 - (N' - (4' - chlorophenyl) - carbamoyloxy) - phenyl) - carbamate.

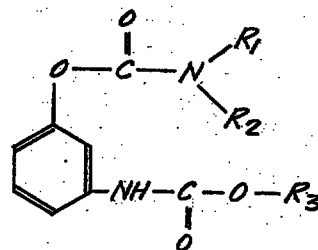
14. n - Propyl N - (3 - (N' - (4' - chloro - phenyl) - carbamoyloxy) - phenyl) - carbamate.

85



15. *n* - Butyl N - (3 - (N' - (4' - chloro - phenyl) - carbamoyloxy) - phenyl) - carbamate.
16. Methyl N - (3 - (N' - (2' - methyl - phenyl) - carbamoyloxy) - phenyl) - carbamate.
17. Ethyl N - (3 - (N' - (2' - methyl - phenyl) - carbamoyloxy) - phenyl) - carbamate.
18. β - Chloroethyl N - (3 - (N' - (2' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
19. Butyn - (1) - yl - (3) N - (3' - (N' - (3'' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
20. Butyn - (1) - yl - (3) N - (3' - (N' - (4'' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
21. Butyn - (1) - yl - (3) N - (3' - (N' - (3'' - trifluoromethylphenyl) - carbamoyloxy) - phenyl) - carbamate.
22. Ethyl N - (3 - (N', N' - diethyl - carbamoyloxy) - phenyl) - carbamate.
23. Ethyl N - (3 - (N', N' - pentamethylene - carbamoyloxy) - phenyl) - carbamate.
24. Ethyl N - (3 - (N' - methylcarbamoyl - oxy) - phenyl) - carbamate.
25. β - Chloroethyl N - (3 - (N' - methyl - carbamoyloxy) - phenyl) - carbamate.
26. *n* - Propyl N - (3 - (N' - methyl - carbamoyloxy) - phenyl) - carbamate.
27. *n* - Butyl N - (3 - (N' - methyl - carbamoyloxy) - phenyl) - carbamate.
28. Methyl N - (3 - (N' - *n* - butyl - carbamoyloxy) - phenyl) - carbamate.
29. Ethyl N - (3 - (N' - *n* - butylcarbamoyl - oxy) - phenyl) - carbamate.
30. sec. - Butyl N - (3 - (N' - *n* - butyl - carbamoyloxy) - phenyl) - carbamate.
31. Methyl N - (3 - (N' - cyclohexyl - carbamoyloxy) - phenyl) - carbamate.
32. Ethyl N - (3 - (N' - cyclohexyl - carbamoyloxy) - phenyl) - carbamate.
33. β - Chloroethyl N - (3 - (N' - cyclohexylcarbamoyloxy) - phenyl) - carbamate.
34. *n* - Propyl N - (3 - (N' - cyclohexyl - carbamoyloxy) - phenyl) - carbamate.
35. *n* - Butyl N - (3 - (N' - cyclohexyl - carbamoyloxy) - phenyl) - carbamate.
36. Ethyl N - (3 - (N' - (3' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
37. β - Chloroethyl N - (3 - (N' - (3' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
38. Methyl N - (3 - (N' - (4' - methyl - phenyl) - carbamoyloxy) - phenyl) - carbamate.
39. Ethyl N - (3 - (N' - (4' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
40. Ethyl N - (3 - (N' - (3' - trifluoro - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
41. β - Chlorethyl N - (3 - (N' - (3' - tri - fluoromethylphenyl) - carbamoyloxy) - phenyl) - carbamate.
42. Butyn - (1) - yl - (3) N - (3' - (N' - methylcarbamoyloxy) - phenyl) - carbamate.
43. Butyn - (1) - yl - (3) N - (3' - (N' - cyclohexylcarbamoyloxy) - phenyl) - carbamate.
44. Butyn - (1) - yl - (3) N - (3' - (N' - phenylcarbamoyloxy) - phenyl) - carbamate.
45. Butyn - (1) - yl - (3) N - (3' - (N' - (2'' - chlorophenyl) - carbamoyloxy) - phenyl) - carbamate.
46. Butyn - (1) - yl - (3) N - (3' - (N' - (4'' - chlorophenyl) - carbamoyloxy) - phenyl) - carbamate.
47. Butyn - (1) - yl - (3) N - (3' - (N' - (2'' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
48. sec. - Butyl N - (3 - (N' - cyclohexyl - carbamoyloxy) - phenyl) - carbamate.
49. Methyl N - (3 - (N' - phenylcarbamoyl - oxy) - phenyl) - carbamate.
50. Ethyl N - (3 - (N' - phenylcarbamoyl - oxy) - phenyl) - carbamate.
51. β - Chlorethyl N - (3 - (N' - phenyl - carbamoyloxy) - phenyl) - carbamate.
52. *n* - Propyl N - (3 - (N' - phenyl - carbamoyloxy) - phenyl) - carbamate.
53. Isopropyl N - (3 - (N' - phenyl - carbamoyloxy) - phenyl) - carbamate.
54. *n* - Butyl N - (3 - (N' - phenyl - carbamoyloxy) - phenyl) - carbamate.
55. sec. - Butyl N - (3 - (N' - phenyl - carbamoyloxy) - phenyl) - carbamate.
56. Methyl N - (3 - (N' - (2' - chloro - phenyl) - carbamoyloxy) - phenyl) - carbamate.
57. Methyl N - (3 - (N' - (3' - methyl - phenyl) - carbamoyloxy) - phenyl) - carbamate.
58. Morpholine - N - carboxylic acid 3 - carbethoxy - aminophenyl ester.
59. Ethyl N - (3 - (N' - (α - naphthyl) - carbamoyloxy) - phenyl) - carbamate.
60. Methyl N - (3 - (N' - (α - naphthyl) - carbamoyloxy) - phenyl) - carbamate.
61. Ethyl N - (3 - (N' - (3', 4' - dichloro - phenyl) - carbamoyloxy) - phenyl) - carbamate.
62. Methyl N - (3 - (N' - methylcarbamoyl - oxy) - phenyl) - carbamate.
63. Methyl N - (3 - (N' - (3', 4' - di - chlorophenyl) - carbamoyloxy) - phenyl) - carbamate.
64. Methyl N - (3 - (N' - (3' - chloro - 4' - methyl) - phenyl) - carbamoyloxy) - phenyl) - carbamate.
65. Ethyl N - (3 - (N' - (3' - chloro - 4' - methylphenyl) - carbamoyloxy) - phenyl) - carbamate.
66. *n* - Propyl N - (3 - (N' - ethyl - carbamoyloxy) - phenyl) - carbamate.
67. *n* - Propyl N - (3 - (N' - *n* - propyl - carbamoyloxy) - phenyl) - carbamate.
68. *n* - Propyl N - (3 - (N' - isopropyl - carbamoyloxy) - phenyl) - carbamate.
69. *n* - Propyl N - (3 - (N' - *n* - butyl - carbamoyloxy) - phenyl) - carbamate.
70. *n* - Butyl N - (3 - (N' - ethylcarbamoyl - oxy) - phenyl) - carbamate.
71. *n* - butyl N - (3 - (N' - isopropyl - carbamoyloxy) - phenyl) - carbamate.
72. *n* - butyl N - (3 - (N' - butyl - carbamoyloxy) - phenyl) - carbamate.
73. Isopropyl N - (3 - (N' - ethylcarbamoyl - oxy) - phenyl) - carbamate.

- oxy) - phenyl) - carbamate.
 74. Isopropyl N - (3 - (N' - isopropyl -
 carbamoyloxy) - phenyl) - carbamate.
 75. Isopropyl N - (3 - (N' - *n* - propyl -
 5 carbamoyloxy) - phenyl) - carbamate.
 76. Isopropyl N - (3 - (N' - *n* - butyl -
 carbamoyloxy) - phenyl) - carbamate.
 77. Isopropyl N - (3 - (N' - cyclohexyl -
 carbamoyloxy) - phenyl) - carbamate.
 10 78. Methyl N - (3 - (N' - ethylcarbamoyl -
 oxy) - phenyl) - carbamate.
 79. Methyl N - (3 - (N' - isopropyl -
 carbamoyloxy) - phenyl) - carbamate.
 80. Methyl N - (3 - N' - *n* propyl -
 15 carbamoyloxy) - phenyl) - carbamate.
 81. Ethyl N - (3 - (N' - ethylcarbamoyl -
 oxy) - phenyl) - carbamate.
 82. Ethyl N - (3 - (N' - isopropylcarbamoyl -
 oxy) - phenyl) - carbamate.
 20 83. Ethyl N - (3 - (N' - *n* - propyl -
 carbamoyloxy) - phenyl) - carbamate.
 84. *n* - Propyl N - (3 - (N' - tert.
 butylcarbamoyloxy) - phenyl) - carbamate.
 85. Ethyl N - (3 - (N' - tert. - butyl -
 25 carbamoyloxy) - phenyl) - carbamate.
 86. Methyl N - (3 - (N' - tert. - butyl -
 carbamoyloxy) - phenyl) - carbamate.
 87. Isopropyl N - (3 - (N' - methyl -
 carbamoyloxy) - phenyl) - carbamate.
 30 88. A process for selectively combating
 weeds in a crop area, wherein there are used
 preparations containing compounds of the
 general formula



in which R₁ represents an alkyl group, a 35
 cycloalkyl group or an aryl group, which last
 may be substituted by a halogen atom and/or
 an alkyl group and/or a trifluoromethyl group,
 R₂ represents a hydrogen atom or an alkyl 40
 group, or R₁ and R₂, together with the nitro-
 gen atom, may form a heterocyclic ring that
 may contain further nitrogen and/or oxygen
 atoms and R₃ represents an alkyl, alkenyl or
 alkynyl group that may be substituted by a 45
 terminal halogen atom.

89. Herbicidal preparations as claimed in
 claim 1, including one or more wetting agents,
 adhesives, emulsifiers and/or dispersing agents.

90. Herbicidal preparations as claimed in
 claim 1, substantially as described in any one 50
 of Examples 3—8 herein.

91. A process as claimed in claim 2, sub-
 stantially as described in Example 1 or 2
 herein.

92. Phenylcarbamates when made by the 55
 process claimed in any one of claims 2—6 or
 91.

ABEL & IMRAY,
 Chartered Patent Agents,
 Quality House, Quality Court,
 Chancery Lane, London W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
 Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
 copies may be obtained.



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