



PATENT SPECIFICATION

NO DRAWINGS

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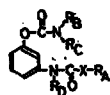
COMPLETE SPECIFICATION

Novel *m*-(Carbamoyloxy) Compounds

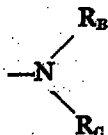
We, SCHERING AKTIENGESELLSCHAFT, a body corporate organised according to the laws of Germany, of 170—172 Mullerstrasse, Berlin N.65, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- 5 This invention relates to novel herbicidal compounds, to new herbicidal compositions and to a new method for the control of undesired plant growth, both pre-emergently and post-emergently, by application of said new and useful herbicidal compositions.

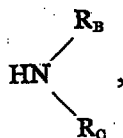
The novel compounds of this invention are *m*-(carbamoyloxy)carbanilates of the following structure:



- 20 wherein R_A is the radical of an alcohol or phenol of the formula $R_A\text{OH}$,



is the radical of a primary or secondary amine of the formula



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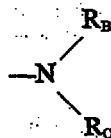
[Price 4s. 6d.]



is the radical of a *m*-aminophenyl of the formula



and X is oxygen or sulfur with the proviso 30 that R_A is not a methyl group when



is a methylamino group and X is oxygen. The substituents R_B and R_C may also form together a heterocyclic ring with the nitrogen to which they are attached, e.g., a morpholine or piperidine compound.

In one useful class of compounds, R_A is an aliphatic hydrocarbon radical, such as an alkyl, alkenyl, or alkynyl radical such as a methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *tert*-butyl, *sec*-butyl, pentyl, 1-ethylpropyl, allyl, 2-methylallyl, 2-butenyl, propynyl or 1-methyl-2-propynyl radical. Compounds having a cyclic R_A group, e.g., cyclohexyl, cyclopropyl, phenyl, or a group containing atoms other than carbon and hydrogen, e.g., a methoxyethyl group, may also be used. Preferably, R_A is an alkyl or alkenyl radical of relatively low molecular weight; thus, when X is oxygen, best results are

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obtained when R_A has less than six carbon atoms, preferably less than five carbon atoms, while when X is sulfur there are preferably less than three carbon atoms, so that in one preferred class $R_A X$ has a molecular weight less than 74.

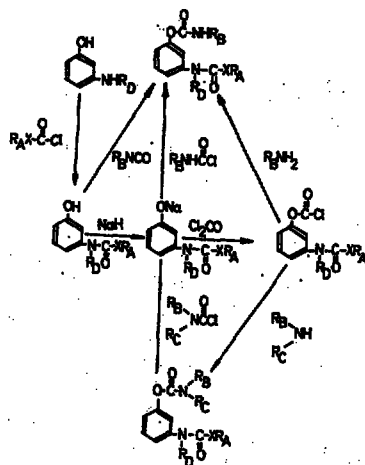
In the preferred types of the compounds of this invention, R_B is a hydrocarbon radical and R_C is hydrogen or a hydrocarbon radical: Examples of such hydrocarbon radicals are alkyl radicals, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *tert*-butyl, *sec*-butyl, pentyl, neopentyl, 1-methylbutyl, isopentyl, hexyl, and 1,1,3,3-tetramethylbutyl, alkenyl radicals such as allyl, 2-methylallyl, 2-butenyl, and 1-ethylallyl, cycloaliphatic radicals such as cyclohexyl or cyclopropyl, and aromatic radicals such as phenyl or tolyl.

Compounds in which there are additional elements (e.g., chlorine or oxygen, as in 2-chloroethyl or 2-methoxyethyl) besides carbon and hydrogen in the R_B or R_C radicals are also within the broad scope of this invention. In a class which is particularly preferred because of its high herbicidal effectiveness, the R_B and R_C substituents are relatively short, e.g., the sum of the lengths of the longest straight chain (or single carbon) of the R_B substituent, and the longest straight chain (or single carbon) of the R_C substituent is at most 4 carbon atoms.

R_D is preferably hydrogen or a methyl group.

Preferably the radicals R_A , R_B , R_C , and R_D contain only carbon and hydrogen atoms.

The novel compounds of this invention may be prepared by methods employed for synthesis of carbamic and carbanilic acid esters. For example, a very useful series of reactions is outlined below:

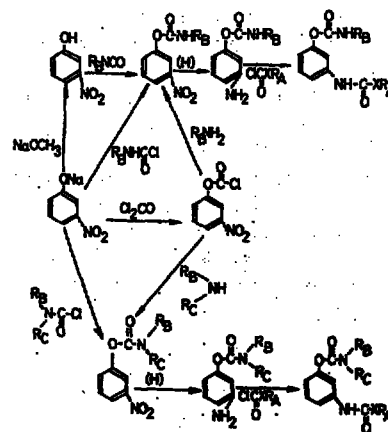


The intermediate *m*-hydroxycarbanilic acid esters may be prepared by treatment of *m*-aminophenol or an *N*-mono-substituted-*m*-aminophenol with the appropriate chloroformate, or chlorothioformate ester in the presence of a suitable acid acceptor.

The reaction of an isocyanate with an appropriate *m*-hydroxycarbanilic acid ester to give the corresponding monosubstituted-carbamate ester may be catalyzed by materials such as triethylamine, 1,4-diazabicyclo [2.2.2] octane, dibutyltin diacetate, dimethyltin dichloride and dibutylbis-(dodecylthio) tin.

Reaction of the sodium salt of a *m*-hydroxycarbanilic acid ester with an *N*-mono-substituted- or an *N,N*-disubstituted-carbamoyl halide will produce the corresponding *m*-((*N*-monosubstituted- or *N,N*-disubstituted-carbamoyl) oxy)-carbanilic acid ester. The same products may be obtained by first treating the sodium salt of a *m*-hydroxycarbanilic acid ester with phosgene to form the chloroformate ester, and reaction of this compound with a primary or secondary amine. The intermediate sodium salt of the *m*-hydroxycarbanilic acid ester is formed in a nonaqueous solvent, using a reagent such as sodium hydride, to avoid hydrolysis of the ester linkage.

Another series of reactions useful for the preparation of these compounds is as follows:



The intermediate *m*-nitrophenyl carbamates are obtained by reaction of *m*-nitrophenol with an appropriate isocyanate, or by reaction of the sodium salt of *m*-nitrophenol with an *N*-monosubstituted- or an *N,N*-disubstituted-carbamoyl halide. They may also be prepared by conversion of *m*-nitrophenol to its chloroformate ester with phosgene, and reaction of this ester with a primary or secondary amine. These *m*-nitrophenyl carbamates are readily reduced to the corresponding *m*-aminophenyl carbamates.

Treatment of the *m*-aminophenyl *N*-mono-substituted- or *N,N*-disubstituted-carbamate with an appropriate chloroformate, or chlorothioformate ester, in the presence of a suitable acid acceptor, will give the desired *m*-[(*N*-monosubstituted- or *N,N*-disubstituted-carbamoyl)oxy] carbanilate ester. Formation of the possible by-product, a urylenediphenylene biscarbamate, is minimized

by slow addition of the *m*-aminophenyl carbamate to a solution of the chloroformate ester, so that the latter is always present in a large excess.

5 Other methods useful for the preparation of *m*-[*N*-substituted-carbamoyloxy] carbanilic acid esters include the reaction of a *m*-hydroxycarbanilic acid ester with an alkyl *N*-substituted-carbamate or an *N*-substituted-urea. The reaction may be driven to completion by removal of the volatile alcohol or ammonia formed. Similarly, reaction of an alkyl carbonate ester of the *m*-hydroxycarbanilate with a primary or secondary amine will yield the desired carbamate and an alcohol. Removal of this alcohol will force the reaction to completion.

20 These reactions of amines with chloroformate esters and of phenols with phosgene, isocyanates, carbamoyl halides and the other reagents described hereinabove are well known in the art. For example, useful procedures for the preparation of carbamic acid and carbanilic acid esters are described by R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry", Ch. 23, John Wiley & Sons, Inc., New York, 1953.

30 Obviously the reactants selected will depend on the final product desired, as will the choice of synthetic procedure used. The *m*-(carbamoyloxy) carbanilate esters thus produced are novel compounds, and are characterized by excellent herbicidal properties.

35 For herbicidal applications, the active *m*-(carbamoyloxy) carbanilate esters as above defined are formulated into herbicidal compositions, by admixture, in herbicidally effective amounts, with the adjuvants and carriers normally employed for facilitating the dispersion of active ingredients for agricultural applications, recognizing the fact that the formulation and mode of application of a toxicant may affect the activity of the material in a given application. Thus, these active herbicidal compounds may be formulated as granules of relatively large particle size, as wettable powders, as emulsifiable concentrates, as powdery dusts, as solutions, or as any of several other known types of formulations, depending on the desired mode of application. Preferred formulations for both pre- and post-emergence herbicidal applications are wettable powders, emulsifiable concentrates, and granules. These formulations may contain as little as 0.5% to as much as 95% or more by weight of active ingredient.

60 Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersant. The wettable powder is ultimately applied to the soil either as a dry dust or as a dispersion in water or other liquid. Typical carriers for wettable powders include fuller's earth, kaolin clays, silicas and other readily wet organic or inorganic diluents. Wettable powders normally

are prepared to contain about 5—95% of active ingredient by weight and usually also contain a small amount of wetting, dispersing or emulsifying agent to facilitate wetting and dispersion. For example, a useful wettable powder formulation contains 80.8 parts by weight of the *m*-(carbamoyloxy) carbanilate ester, 17.9 parts by weight of palmetto clay, and 1.0 part by weight of sodium lignosulfate and 0.3 part by weight of sulfonated aliphatic polyester as wetting agents.

70 Emulsifiable concentrates are homogeneous liquid compositions which are dispersible in water or other dispersant, and may consist entirely of the *m*-(carbamoyloxy) carbanilate ester with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone and other non-volatile organic solvents. For herbicidal application these concentrates are dispersed in water or other liquid carrier, and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises 0.5 to 95% of active ingredient by weight of the herbicidal composition. For example, a useful emulsifiable concentrate formulation contains 11.6 parts by weight of the *m*-(carbamoyloxy) carbanilate ester 57.7 parts by weight of cresol, and 30.7 parts by weight of sulfated ethoxylated nonylphenol.

100 Granular formulations, wherein the toxicant is carried on relatively coarse particles, are usually applied without dilution to the area in which suppression of vegetation is desired. Typical carriers for granular formulations include sand, fuller's earth, bentonite clays, vermiculite, perlite and other organic or inorganic materials which absorb or which may be coated with the toxicant. Granular formulations normally are prepared to contain about 5—25% of active ingredient and may also contain small amounts of other ingredients which may include surface-active agents such as wetting agents, dispersing agents or emulsifiers; oils such as heavy aromatic naphthas, kerosene or other petroleum fractions, or vegetable oils; and/or stickers such as dextrans, glue or synthetic resins. The average particle size of the granules is usually between 150 and 2400 microns. For example, a useful granular formulation contains 5.05 parts by weight of the *m*-(carbamoyloxy) carbanilate ester, 5.00 parts by weight of corn oil, and 89.95 parts by weight of crushed corn cobs.

115 Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; polyhydric alcohols; and other types of surface-active agents, many of which are available in commerce. The surface-active agent, when used, normally comprises from 0.1% to 130

15% by weight of the herbicidal composition.

5 Dusts, which are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours, and other organic and inorganic solids which act as dispersants and carriers for the toxicant, are useful formulations for soil-incorporated applications; the finely divided solids have an average particle size of less than about 50 microns.

10 Pastes, which are homogeneous suspensions of a finely divided solid toxicant in a liquid carrier such as water or oil, are employed for specific purposes. These formulations normally contain about 5—95% of active ingredient by weight, and may also contain small amounts of a wetting, dispersing or emulsifying agent to facilitate dispersion. For application, the pastes are normally diluted and applied as a spray to the area to be affected.

20 Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a dispersant in which it

is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene or other organic solvents. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freons (FREON is a Trade Mark), may also be used. 30

The following Examples, in which all temperatures are in degrees Centigrade, are given to illustrate this invention further. To save space the methods of preparation of most of the tabulated compounds are given by reference to certain typical detailed procedures. It will, of course, be understood by those skilled in the art that for each method an appropriate change in the starting materials should be made in order to obtain the desired compound, thus, in making the *m*-propylcarbamoyl compound of Example 3 by the method of Example 2, propyl isocyanate will be used in place of the ethyl isocyanate of Example 2. 40

Example	Compound	Melting Point	Synthesis Procedure
Experiment	methyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	131°	See below
1	methyl <i>m</i> -[(ethylcarbamoyl)oxy] carbanilate	156—7°	See below
2.	methyl <i>m</i> -[(propylcarbamoyl)oxy] carbanilate	148.5—9.5°	As in Ex. 1 but using 1,4-diazabicyclo (2.2.2) octane as the amine catalyst.
3.	methyl <i>m</i> -[(isopropylcarbamoyl)oxy] carbanilate	167—8°	As in Ex. 2.
4.	methyl <i>m</i> -[(butylcarbamoyl)oxy] carbanilate	117—8°	As in Ex. 2.
5.	methyl <i>m</i> -[(<i>tert</i> -butylcarbamoyl)oxy] carbanilate	162—3°	As in Ex. 2.
6.	methyl <i>m</i> -[(isobutylcarbamoyl)oxy] carbanilate	142—3°	As in Ex. 2.
7.	methyl <i>m</i> -[(<i>sec</i> -butylcarbamoyl)oxy] carbanilate	144.5—5.5°	As in Ex. 2.
8.	methyl <i>m</i> -[(allylcarbamoyl)oxy] carbanilate	147—8°	See below
9.	methyl <i>N</i> -methyl- <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	boils at 85° (at 5×10 ⁻⁵ mm Hg A)	See below
10.	methyl <i>m</i> -[(dimethylcarbamoyl)oxy] carbanilate	145.0—5.5°	See below
11.	methyl <i>m</i> -[(diethylcarbamoyl)oxy] carbanilate	94—5°	See below
12.	methyl <i>m</i> -[(2-methylallyl)carbamoyl]oxy] carbanilate	127.5—8.5°	See below
13.	<i>sec</i> -butyl <i>m</i> -[(dimethylcarbamoyl)oxy] carbanilate	92.5—4.0°	See below
14.	<i>S</i> -methyl <i>m</i> -[(methylcarbamoyl)oxy] thiocarbanilate	153.5—4.5°	See below
15.	isopropyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	158.0—9.5°	As in Experiment.

Example	Compound	Melting Point	Synthesis Procedure
16.	methyl <i>m</i> -[(cyclohexylcarbamoyl)oxy] carbanilate	166—7°	See below
17.	methyl <i>m</i> -[(phenylcarbamoyl)oxy] carbanilate	154—5°	As in Ex. 2.
18.	allyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	124.5—5.5°	Crude intermediate made as in Experiment dissolved in ether, extracted with dilute hydrochloric acid and with water; ether solution concentrated to dryness, and solid recrystallized from benzene-petroleum ether mixture. Intermediate then reacted as in Example 1.
19.	allyl <i>m</i> -[(<i>tert</i> -butylcarbamoyl)oxy] carbanilate	155—6°	As in Ex. 2.
20.	ethyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	136—7°	Intermediate as in Experiment reacted as in Example 16.
21.	propyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	128.5—30.0°	As in Ex. 20.
22.	butyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	113.5—4.5°	As in Ex. 20.
23.	isobutyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	133—4°	As in Ex. 22.
24.	<i>sec</i> -butyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	126.5—7.5°	As in Ex. 22.
25.	<i>tert</i> -butyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	157—8°	See below
26.	<i>sec</i> -butyl <i>m</i> -[(<i>tert</i> -butylcarbamoyl)oxy] carbanilate	140.0—40.5°	As in Ex. 1.
27.	methyl <i>m</i> -[(hexylcarbamoyl)oxy] carbanilate	115.5—6.5°	See below
28.	methyl <i>m</i> -[(1,1,3,3-tetramethylbutyl) carbamoyl] oxy] carbanilate	152.0—2.5°	See below
29.	allyl <i>m</i> -[(allylcarbamoyl)oxy] carbanilate	105.5—6.0°	As in Ex. 27.
30.	<i>sec</i> -butyl <i>m</i> -[(isopropylcarbamoyl)oxy] carbanilate	151.5—2.0°	As in Ex. 16.
31.	pentyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	106.5—7.5°	See below
32.	1-methylbutyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	115.5—6.0°	As in Ex. 31.
33.	1-ethylpropyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	129—30°	Intermediate as in Experiment reacted as in Example 31.
34.	1,2-dimethylpropyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	143—4°	As in Ex. 33.

Example	Compound	Melting Point	Synthesis Procedure
35.	2-methylallyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	126—7°	See below
36.	2-propynyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	128—9°	As in Ex. 35.
37.	methyl <i>m</i> -[(dimethylcarbamoyl)oxy]- <i>N</i> -methylcarbanilate	71—3° (78—9° after sublimation)	See below
38.	methyl <i>m</i> -[(diisopropylcarbamoyl)oxy] carbanilate	113—4°	As in Ex. 37.
39.	methyl <i>m</i> -[(butylmethylcarbamoyl)oxy] carbanilate	86—8°	As in Ex. 37.
40.	<i>sec</i> -butyl <i>m</i> -[(diethylcarbamoyl)oxy] carbanilate	58—60°	As in Ex. 37.
41.	<i>S</i> -ethyl <i>m</i> -[(methylcarbamoyl)oxy] thiocarbanilate	154—5°	As in Ex. 14.
42.	methyl <i>m</i> -[(<i>m</i> -chlorophenyl)carbamoyl]oxy] carbanilate	159—61°	As in Ex. 16.
43.	cyclohexyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate		See below
44.	phenyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	163.0—3.5°	Intermediate made as in Ex. 43, reacted as in Example 16.
45.	2-methoxyethyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	84—5°	As in Ex. 35.
46.	benzyl <i>m</i> -[(methylcarbamoyl)oxy] carbanilate	120.0—20.5°	See below

EXPERIMENT

5 To a solution of 43.6 g of *m*-aminophenol in 250 ml of dry acetonitrile was added 18.9 g of methyl chloroformate at a rate which maintained the temperature of the solution below 40°. The resultant mixture was stirred for one hour at room temperature and for two hours at reflux temperature, then cooled. The precipitate of *m*-aminophenol hydrochloride was removed by filtration and the filtrate was evaporated to dryness. The crude product was recrystallized from water to yield 11.0 g of

the intermediate, methyl *m*-hydroxycarbanilate melting at 94—6°.

15 To a stirred solution of 5.5 g of methyl *m*-hydroxycarbanilate and two drops of triethylamine in 75 ml of ether, 2.3 g of methyl isocyanate was added dropwise. The mixture was stirred and refluxed for 18 hours and cooled. The white crystalline product was isolated by filtration. A yield of 4.5 g of methyl *m*-[(methylcarbamoyl)oxy] carbanilate, melting at 130—2°, was obtained. On recrystallization from toluene, this ester melted 25 at 131°.

Analysis:

Calculated for $C_{10}H_{12}N_2O_4$: C 53.36, H 5.39, N 12.49;
Found: C 53.80, H 5.57, N 12.45.

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EXAMPLE 1.

A mixture of 25.0 g of methyl *m*-hydroxycarbanilate, 11.2 g of ethyl isocyanate, and five drops of triethylamine was heated in a stoppered flask at 60° for three hours, cooled,

and the crude product was recrystallized from ethyl acetate to yield 24.3 g of solid melting at 146—50°. Recrystallization from toluene gave methyl *m*-[(ethylcarbamoyl)oxy] carbanilate melting at 156—7°.

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Analysis:

Calculated for $C_{11}H_{14}N_2O_4$: C 55.45, H 5.92, N 11.76;
Found: C 55.57, H 5.98, N 11.52.

EXAMPLE 8.

Allyl isocyanate (16.4 g) was added dropwise to a solution of 30.0 g of methyl *m*-hydroxycarbanilate and 2.1 g of 1,4-diazabicyclo[2.2.2]octane in 300 ml of ethyl acetate. The reaction mixture was heated at

60° for three hours, cooled, and filtered to yield 35.7 g of crude product. Recrystallization from ethyl acetate or from methanol gave methyl *m*-[(allylcarbamoyl)oxy] carbanilate melting at 147—8°.

Analysis:

Calculated for $C_{12}H_{14}N_2O_4$: C 57.59, H, 5.64, N 11.20;
Found: C 57.61, H 5.74, N 10.91.

EXAMPLE 9.

The intermediate methyl *m*-hydroxy-*N*-methylcarbanilate was prepared as follows: Methyl chloroformate (14.2 g) was added dropwise to a solution of 36.9 g of *m*-(methylamino)phenol in 300 ml of acetonitrile, maintaining the temperature at 25°. When the addition was complete, the mixture was heated to 55°, stirred at this temperature for 2.5 hours, and cooled to room temperature. The acetonitrile was removed under reduced pressure and the residual oil was dissolved by

addition of 500 ml of water and 500 ml of ether. The aqueous layer was extracted with ether and the combined ether layers were washed with a 5% hydrochloric acid solution and with water. After drying the ether solution over magnesium sulfate, the ether was evaporated to yield 20 g of light yellow oil. A small portion of this crude methyl *m*-hydroxy-*N*-methylcarbanilate was distilled to obtain an analytical sample boiling at 80° (5×10^{-4} mm).

Analysis:

Calculated for $C_9H_{11}NO_3$: C 59.66, H 6.12, N 7.73;
Found: C 59.76, H 6.24, N 7.92.

Methyl isocyanate (5.0 g) was added dropwise to a solution of the crude 14.5 g methyl *m*-hydroxy-*N*-methylcarbanilate and 20 drops of triethylamine in 150 ml of benzene. The reaction mixture was stirred at room temperature for 1.5 hours and heated at 57°

for three hours. The solvent was removed to yield 18.9 g of crude methyl *N*-methyl-*m*-[(methylcarbamoyl)oxy] carbanilate, a yellow oil. A small portion of this oil was distilled to give an analytical sample boiling at 85° (5×10^{-4} mm).

Analysis:

Calculated for $C_{11}H_{14}N_2O_4$: C 55.45, H 5.92, N 11.76;
Found: C 55.35, H 6.09, N 11.81.

EXAMPLE 10.

m-Nitrophenol (100.0 g) was added portionwise to a solution of 38.8 g of sodium methoxide in 300 ml of methanol, the solution was heated at 60—65° for 1.5 hour, then evaporated to dryness. This sodium salt of *m*-nitrophenol (111.0 g) was dissolved in 700 ml of dioxane, and 67.3 g of dimethylcarbamoyl chloride was added dropwise over a one-half hour period. The reaction mixture was heated at 60—65° for two hours, stirred overnight at room temperature, then poured into 3300 ml of water. After stirring for one hour the crude *m*-nitrophenyl dimethylcarbamate (107.0 g, m.p. 48—55°) was isolated by filtration, and dissolved in 600 ml of ethyl acetate. Platinum oxide (0.4 g) was added and the mixture was hydrogenated in a Parr hydrogenation appa-

ratus until the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration and the filtrate was concentrated to dryness. The residual yellow oil solidified on standing and was recrystallized from a benzene-petroleum ether mixture to yield 80.0 of *m*-aminophenyl dimethylcarbamate melting at 80—6°.

To a solution of 9.9 g of methyl chloroformate in 50 ml of benzene, a solution of 18.0 g of the *m*-aminophenyl dimethylcarbamate and 10.1 g of triethylamine in 175 ml of benzene was added dropwise, maintaining the temperature of the reaction at 25—30°. After the addition was complete, the mixture was stirred for one hour at 40° and for one hour at room temperature, then poured into 250 ml of ether. The solid was collected

by filtration, washed with water to remove the amine hydrochloride, yielding 11.9 g of crude methyl *m* - [(dimethylcarbamoyl)oxy] carbanilate melting at 144—5°. An additional

3.5 g of product was obtained by concentration of the filtrate. Recrystallization from benzene-hexane mixture raised the melting point to 145.0—5.5°. 5

Analysis:

10 Calculated for $C_{11}H_{14}N_2O_4$: C 55.45, H 5.92, N 11.76;
Found: C 55.57, H 6.03, N 11.79.

EXAMPLE 11.

A suspension of 4.6 g of sodium hydride in oil was added slowly to a solution of 16.7 g of methyl *m*-hydroxycarbanilate in 50 ml of *N,N*-dimethylformamide and 200 ml of xylene, maintaining the temperature at 30—35°. The mixture was stirred for one hour, then 13.6 g of diethylcarbamoyl chloride was added dropwise, maintaining the temperature at 30—35°. When the addition was complete, the reaction mixture was heated for one hour

at 55—60°, cooled, and the precipitate of sodium chloride removed by filtration. The filtrate was concentrated to dryness, the residue was washed with pentane, and triturated with water to give a crude solid product. After filtration and recrystallization from aqueous methanol, a yield of 16.2 g of methyl *m*-[(diethylcarbamoyl)oxy] carbanilate was obtained. A small portion was distilled at 120° (0.015 mm) to give an analytical sample melting at 94—5°. 25 30

Analysis:

35 Calculated for $C_{13}H_{18}N_2O_4$: C 58.63, H 6.81, N 10.52;
Found: C 58.58, H 6.74, N 10.76.

EXAMPLE 12.

Methyl *m*-hydroxycarbanilate (33.4 g) was converted to the sodium salt with sodium hydride as described in Example 12. This sodium salt was added portionwise to a solution of 19.8 g of phosgene in 300 ml of ethyl acetate, maintaining the temperature at -5 to 0°. The mixture was stirred for one hour as it warmed to room temperature, then filtered to yield 44 g of the chloroformate ester of methyl *m*-hydroxycarbanilate.

2-Methylallylamine (28.4 g) was added

dropwise to a solution of 45.9 g of the chloroformate ester of methyl *m*-hydroxycarbanilate in 300 ml of ethyl acetate, maintaining the temperature at 25—30°. The mixture was stirred for one hour and allowed to stand overnight. The precipitate of amine hydrochloride was removed by filtration and the filtrate was concentrated to dryness. The crude methyl *m* - [(2-methylallyl)carbamoyl]oxy] carbanilate was recrystallized several times from a benzene-hexane mixture to obtain a sample melting at 127.5—8.5°. 50 55 60

Analysis:

Calculated for $C_{13}H_{18}N_2O_4$: C 59.08, H 6.10, N 10.60;
Found: C 59.29, H 6.27, N 10.78.

EXAMPLE 13.

A solution of 18.0 g of *m*-aminophenyl dimethylcarbamate (see Ex. 11) and 10.1 g of triethylamine in 200 ml of benzene was added to a solution of 14.3 g of *sec*-butyl chloroformate in 50 ml of benzene, maintaining the temperature at 25—30°. The mixture was stirred for one hour at 45—50°, and allowed to stand over the weekend. The amine hydrochloride was removed by filtration and the filtrate was concentrated to dryness. The resi-

dual oil was dissolved in ether and the ether layer was washed with a cold 5% solution of hydrochloric acid and with water. After drying the solution over magnesium sulfate, the ether was removed to give a red oil which crystallized on standing. After recrystallization from a benzene-hexane mixture, a yield of 13.5 g of *sec*-butyl *m*-[(dimethylcarbamoyl)oxy] carbanilate, melting at 92.5—4.0°, was obtained. 75 80

85 Analysis:

Calculated for $C_{14}H_{20}N_2O_4$: C 59.98, H 7.19, N 9.99;
Found: C 59.94, H 7.06, N 10.13.

EXAMPLE 14.

A solution of 43.6 g of *m*-aminophenol in 300 ml of acetonitrile was warmed to 35°, and 22.0 g of *S*-methyl chlorothioformate was added dropwise. The temperature of the mixture rose to 55°. The mixture was stirred for two hours at 70°, cooled to room tem-

perature, and the precipitate (*m*-aminophenol hydrochloride) was removed by filtration. Concentration of the filtrate gave 36.1 g of crude *S*-methyl *m*-hydroxythiocarbanilate melting at 135—9°. Two recrystallizations from aqueous methanol raised the melting point to 139—40°.

15 Analysis:

Calculated for $C_8H_9NO_2S$: C 52.44, H 4.95, N 7.65;
Found: C 52.31, H 5.07, N 7.52.

20 Methyl isocyanate (4.85 g) was added dropwise to a stirred suspension of 15.5 g of *S*-methyl *m*-hydroxythiocarbanilate and 25 drops of triethylamine in 150 ml of benzene. When the addition was complete, the mixture was heated to 70° for two hours, then cooled. The crude product was isolated by filtration

and recrystallized from aqueous methanol to yield 13.4 g of white crystals melting at 153—8°. A second recrystallization of the *S*-methyl *m*-[(methylcarbamoyl)oxy]thiocarbanilate produced a sample melting at 153.5—4.5°.

Analysis:

Calculated for $C_{10}H_{12}N_2O_3S$: C 49.98, H 5.03, N 11.66;
Found: C 49.71, H 4.77, N 11.79.

EXAMPLE 16.

35 Cyclohexyl isocyanate (11.8 g) was added dropwise to a solution of 15.0 g of methyl *m*-hydroxycarbanilate and 1.1 g of 1,4-diazabicyclo[2.2.2]octane in 150 ml of benzene. The mixture was refluxed for one hour, cooled,

and filtered. The white solid was recrystallized several times from aqueous methanol to yield 14.0 g of methyl *m*-[(cyclohexylcarbamoyl)oxy] carbanilate melting at 166—7°.

45 Analysis:

Calculated for $C_{15}H_{20}N_2O_4$: C 61.63, H 6.90, N 9.58;
Found: C 61.83, H 7.13, N 9.83.

EXAMPLE 25.

50 A solution of *m*-aminophenol in 450 ml of acetonitrile was added dropwise to a stirred solution of 54.6 g of *tert*-butyl chloroformate in 200 ml of acetonitrile, maintaining the temperature of the reaction mixture below 0°. When the addition was complete, the mixture was allowed to warm to room temperature, stirred for three hours, and allowed to stand for 48 hours. The mixture was filtered to remove the *m*-aminophenol hydrochloride,

and the filtrate was concentrated to dryness. The residue was extracted with ether, the insoluble *m*-aminophenol was removed, and the ether solution was extracted with cold 5% hydrochloric acid solution and with water. The ether layer was dried over magnesium sulfate, evaporated to dryness and the residual solid recrystallized from aqueous methanol to yield 13.5 g of *tert*-butyl *m*-hydroxycarbanilate melting at 135.0—5.5°.

Analysis:

70 Calculated for $C_{11}H_{15}NO_3$: C 63.14, H 7.23, N 6.69;
Found: C 62.99, H 7.48, N 6.90.

This intermediate was reacted with methyl isocyanate, following the procedure described in Example 17, to yield *tert*-butyl *m*-[(methyl-

carbamoyl)oxy] carbanilate, melting at 157—8°.

Analysis:

Calculated for $C_{13}H_{13}N_2O_4$: C 58.63, H 6.81, N 10.52;

Found: C 58.65, H 6.70, N 10.76.

EXAMPLE 27.

- 5 Hexyl isocyanate (13.4 g) was added dropwise to a stirred solution of 16.7 g of methyl *m*-hydroxycarbanilate and 25 drops of triethylamine in 200 ml of benzene, and the reaction mixture was stirred for nine hours

at room temperature. The crude methyl *m*-
10 [(hexylcarbamoyl)oxy] carbanilate was isolated by filtration and recrystallized from aqueous methanol to yield 24.2 g of pure product melting at 115.5—6.5°.

- 15 Analysis:

Calculated for $C_{16}H_{22}N_2O_4$: C 61.20, H 7.53, N 9.52;

Found: C 61.19, H 7.40, N 9.27.

EXAMPLE 28.

- 20 The reactants, 12.5 g of methyl *m*-hydroxycarbanilate, 1.0 g of 1,4-diazabicyclo[2.2.2]octane, and 12.3 g of 1,1,3,3-tetramethylbutyl isocyanate, were mixed by hand, and the mixture was heated in a stoppered flask at 60° for eight hours. Hexane (100 ml) was added,
25 the mixture was filtered, and the crude solid product was dissolved in 500 ml of ethylacetate and 100 ml of ether. The solution

was washed with a cold 5% solution of sodium hydroxide and with water, dried over magnesium sulfate, and concentrated to dryness. The residue was recrystallized from aqueous methanol to yield 10.0 g of methyl *m*-
30 [(1,1,3,3-tetramethylbutyl)carbamoyl]oxy] carbanilate, melting at 150—1°. A second recrystallization from aqueous methanol
35 raised the melting point to 152.0—2.5°.

Analysis:

Calculated for $C_{17}H_{26}N_2O_4$: C 63.33, H 8.13, N 8.69;

Found: C 63.57, H 7.89, N 8.73.

EXAMPLE 31.

- 40 Pentyl chloroformate (30.1 g) was added dropwise to a solution of 43.6 g of *m*-aminophenol in 300 ml of acetonitrile. The reaction was exothermic and the temperature
45 had risen to 42° by the time the addition was complete. The reaction mixture was heated to 76°, maintained at that temperature for one hour, then allowed to cool to room temperature. The mixture was poured

into ice water and the water extracted with ether. The ether solution was washed with 10% hydrochloric acid solution and with water, dried over magnesium sulfate and concentrated to dryness. The residual solid was
50 recrystallized from a benzene-hexane mixture to yield 28.7 g of pentyl *m*-hydroxycarbanilate
55 melting at 80.0—81.5°. Further recrystallization from benzene raised the melting point to 82.5—3.0°.

- 60 Analysis:

Calculated for $C_{12}H_{17}NO_3$: C 64.55, H 7.68, N 6.27;

Found: C 64.66, H 7.38, N 6.50.

- 65 Methyl isocyanate (4.9 g) was added dropwise to a stirred mixture of 16.7 g of pentyl *m*-hydroxycarbanilate and 25 drops of triethylamine in 200 ml of benzene. When the addition was complete, the solution was heated to 65° and maintained at this tem-

perature for two hours, then allowed to cool. The white solid was collected by filtration and recrystallized from aqueous methanol to yield
70 17.3 g of pentyl *m*-[(methylcarbamoyl)oxy] carbanilate melting at 106.5—7.5°.

Analysis:

- 75 Calculated for $C_{14}H_{20}N_2O_4$: C 59.98, H 7.19, N 9.99;

Found: C 60.19, H 7.09, N 10.19.

EXAMPLE 35.

2-Methylallyl chloroformate (26.8 g) was added dropwise to a solution of 43.6 g of *m*-aminophenol in 300 ml of acetonitrile. The temperature rose to 62° during the addition and a solid settled out of the solution. The slurry was heated at 70° for two hours, cooled to room temperature, and filtered. The filtrate was concentrated to dryness, the residual oil was dissolved in benzene, and the benzene

solution was washed with 10% hydrochloric acid solution and with water. After drying the solution over magnesium sulfate, the benzene was removed under reduced pressure, to yield a brown oil which crystallized on standing. Recrystallization from a benzene-petroleum ether mixture produced 17.3 g of 2 - methylallyl *m*-hydroxycarbanilate melting at 66—7°. A second recrystallization from the same solvent raised the melting point to 68—9°.

Analysis:

Calculated for $C_{11}H_{13}NO_3$: C 63.75, H 6.32, N 6.76;
Found: C 64.04, H 6.49, N 7.03.

This intermediate was reacted with methyl isocyanate, following the procedure described in Example 32, to yield 2-methylallyl *m*-

[(methylcarbamoyl)oxy] carbanilate melting at 126—7° after recrystallization from aqueous methanol.

Analysis:

Calculated for $C_{13}H_{16}N_2O_4$: C 59.08, H 6.10, N 10.60;
Found: C 58.83, H 6.34, N 10.83.

EXAMPLE 37.

A suspension of 4.0 g of sodium hydride in oil was added portionwise to a solution of 15.5 g of methyl *m* - hydroxy - *N* - methylcarbanilate in 40 ml of *N,N* - dimethylformamide and 160 ml of xylene. The mixture was stirred at 55—60° for one hour, cooled to 22°, and 9.3 g of dimethylcarbamoyl chloride was added dropwise over a 15 minute period. The reaction mixture was stirred at room temperature overnight, then filtered to remove the precipitate of sodium chloride. The filtrate was evaporated to dry-

ness, the residual oil dissolved in ether, and the ether solution washed with a cold 5% solution of sodium hydroxide and with water. After drying over magnesium sulfate, the ether was removed and the residual semi-solid was thoroughly washed with pentane to remove the oil. The crude product was recrystallized from a benzene-hexane mixture to yield methyl *m* - [(dimethylcarbamoyl) oxy] - *N*-methylcarbanilate melting at 71—3°. A small portion was sublimed at 80° (0.1 mm) to give an analytical sample melting at 78—9°.

Analysis:

Calculated for $C_{12}H_{16}N_2O_4$: C 57.13, H 6.39, N 11.11;
Found: C 57.22, H 6.63, N 11.28.

EXAMPLE 43.

Cyclohexyl chloroformate (60.2 g) was added dropwise to a solution of 87.3 g of *m*-aminophenol in 700 ml of acetonitrile, maintaining the temperature below 32°. When the addition was complete, the mixture was refluxed for two hours, cooled, and filtered. The solid was washed with water to remove

the amine hydrochloride, leaving 61.4 g of crude product. An additional 17.1 g of product were obtained by evaporation of the filtrate. The combined samples were recrystallized from aqueous methanol, and from an ethyl acetate-toluene mixture, to yield 52.6 g of cyclohexyl *m*-hydroxycarbanilate melting at 179—80°.

Analysis:

Calculated for $C_{13}H_{17}NO_3$: C 66.36, H 7.28, N 5.95;
Found: C 66.43, H 7.32, N 6.16.

Methyl isocyanate (9.0 g) was added dropwise to a solution of 35.3 g of cyclohexyl *m*-

hydroxycarbanilate and six drops of triethylamine in 300 ml of ethyl acetate. The mix-

ture was refluxed for one hour, then concentrated to dryness. A yield of 20.9 g of cyclohexyl *m*-[(methyl-[(methoxycarbonyl)oxy]-

carbanilate was obtained by recrystallization of the crude product from aqueous methanol and from ethyl acetate.

Analysis:

Calculated for $C_{16}H_{20}N_2O_4$: C 61.63, H 6.90, N 9.58;
Found: C 61.74, H 7.17, N 9.46.

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EXAMPLE 46.

Benzyl chloroformate (34.1 g) was added dropwise to a stirred solution of 43.6 g of *m*-aminophenol in 300 ml of acetonitrile. The temperature, which rose to 40° during the addition, was increased to 55–60° and maintained there for two hours. After cooling, the mixture

was poured into 1200 ml of ice-water, the suspension was stirred for one hour, and the crude product was collected by filtration and recrystallized from a benzene-hexane mixture. A yield of 37.1 g of benzyl *m*-hydroxycarbanilate, melting at 126–7° was obtained. A second recrystallization from benzene raised the melting point to 127.5–8.0°.

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Analysis:

Calculated for $C_{14}H_{13}NO_3$: C 69.12, H 5.39, N 5.76;
Found: C 68.90, H 5.09, N 6.02.

This intermediate was reacted with methyl isocyanate, following the procedures described in Example 32, to yield benzyl *m*-[(methyl-

carbamoyl)oxy] carbanilate melting at 120.0–20.5° after recrystallization from aqueous methanol.

Analysis:

Calculated for $C_{16}H_{19}N_2O_4$: C 63.99, H 5.37, N 9.33;
Found: C 64.20, H 5.12, N 9.20.

The compounds of Examples 1–46 were all tested for pre-emergence and post-emergence effectiveness with a variety of plants at dosages of 6 pounds per acre of these toxicants. All were found to have significant herbicidal properties. Typically the pre-emergence herbicidal activity of the toxicant was demonstrated as follows:

In flat pans was placed, to a depth of three inches, a 1:1 mixture of silt loam and sandy loam soil. In the soil were then planted seeds of crabgrass (*Digitaria sanguinalis*), German hay millet (*Setaria italica*), yellow foxtail (*Setaria glauca*), flax (*Linum usitatissimum*), mustard (*Brassica juncea*), and lettuce (*Lactuca sativa*), at a depth of one-fourth to one-half inch. As soon as the seeds were planted and the flats watered, the toxicant was sprayed on the soil as an acetone-water solution, at a rate equivalent to six pounds of toxicant per acre. Both the treated flats and an untreated control were held in the greenhouse for approximately three weeks, after which time the performance of the toxicant was assessed in terms of percent kill with respect to the untreated control.

The post-emergence herbicidal activity of the toxicant was demonstrated as follows: In

flat pans was placed, to a depth of three inches, a 1:1 mixture of silt loam and sandy loam soil. In the soil were then planted seeds of corn (*Zea mays*), pea (*Pisum sativum*), peanut (*Arachis hypogaea*), cotton (*Gossypium hirsutum*), and soybean (*Glycine max*), at a depth of approximately one inch, and seeds of oats (*Avena sativa*), flax (*Linum usitatissimum*), mustard (*Brassica juncea*), lettuce (*Lactuca sativa*), tomato (*Lycopersicon esculentum* Mill.), pigweed (*Amaranthus retroflexus*), crabgrass (*Digitaria sanguinalis*), barnyard grass (*Echinochloa crusgalli*), carrot (*Daucus carota*), cucumber (*Cucumis sativus*), safflower (*Carthamus tinctorius*), at a depth of one-fourth to one-half inch. The flats were watered, and the seeds allowed to grow in the greenhouse for two weeks. Maintaining an untreated control, the stand of plants was then sprayed with a solution of the toxicant in aqueous acetone, at a rate equivalent to six pounds of toxicant per acre. Both treated and untreated plants were held in the greenhouse for two to three weeks, after which the number of surviving plants were counted, and the percent kill with respect to the untreated control was determined.

Other examples of compounds falling with-

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in the generic formulae presented herein, which may be formulated into herbicidal compositions and applied as herein illustrated are:

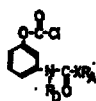
- 5 methyl *m*-[(cyclopropylcarbamoyl)oxy] carbanilate
ethyl *m*-[(*tert*-butylcarbamoyl)oxy] carbanilate
cyclopropyl *m*-[(isopropylcarbamoyl)oxy] carbanilate
10 propyl *m*-[(*tert*-butylcarbamoyl)oxy] carbanilate
butyl *m*-[(*tert*-butylcarbamoyl)oxy] carbanilate
methyl *m*-[(neopentylcarbamoyl)oxy] carbanilate
15 methyl *m*-[(*tert*-butylcarbamoyl)oxy] - *N*-methylcarbanilate
methyl *m*-[(piperidinocarbonyl)oxy] carbanilate
20 methyl *m*-[(*tert*-butylmethylcarbamoyl)oxy] carbanilate
ethyl *m*-[(ethylisopropylcarbamoyl)oxy] carbanilate
S - methyl *m*-[(*tert*-butylcarbamoyl)oxy] thiocarbanilate
25 methyl *N*-ethyl - *m*-[(methylcarbamoyl)oxy] carbanilate
S - methyl *m*-[(isopropylcarbamoyl)oxy] thiocarbanilate
30 ethyl *m*-[(2-methylallyl)carbamoyl]oxy] carbanilate

It is clear that the classes of *m*-(carbamoyloxy)-carbanilate esters described and illustrated herein are characterized by herbicidal activity, and that the degree of this activity varies among specific compounds within these classes and to some extent among the species of plant to which these compounds may be applied. Thus, selection of a specific herbicidal compound to control undesirable plant species without injury to a desired crop species may readily be made.

The active herbicidal compounds of this invention may be formulated and/or applied with insecticides, fungicides, nematocides, plant growth regulators, fertilizers, and other agricultural chemicals and may be used as effective soil sterilants as well as in herbicidal applications. In applying an active compound of this invention, whether formulated alone or with other agricultural chemicals, an effective amount and concentration of the *m*-[(*N*-substituted-carbamoyl)oxy] carbanilate ester is of course employed.

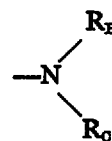
55 WHAT WE CLAIM IS:—

1. Herbicidal *m*- (carbamoyloxy) carbanilates of the formula:—

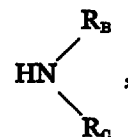


wherein R_A is the radical of an alcohol or phenol of the formula R_AOH ,

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is the radical of a primary or secondary amine of the formula:—



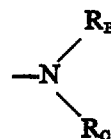
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is the radical of a *m*-aminophenol of the formula:—



and X is oxygen or sulfur with the proviso that R_A is not a methyl group when

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is a methylamino group and X is oxygen.

2. Compounds as claimed in claim 1 in which R_A is an aliphatic hydrocarbon radical.

3. Compounds as claimed in any preceding claim in which R_A , R_B , R_C and R_D contain only carbon and hydrogen.

4. Compounds as claimed in any preceding claim in which R_B is a hydrocarbon radical and R_C is hydrogen or a hydrocarbon radical.

5. Compounds as claimed in any preceding claim in which R_D is a hydrogen atom or a methyl group.

6. Compounds as claimed in claim 4 or 5 in which the sum of the lengths of the longest straight chain, or single carbon, of the R_B substituent and the longest straight chain, or single carbon, of any R_C substituent is at most four carbon atoms.

7. Compounds as claimed in any of claims 4 to 6 in which R_A is an aliphatic hydrocarbon radical of one to four carbon atoms and X is oxygen.

8. Compounds as claimed in claim 7 in which R_A is alkyl of one to four carbons and X is oxygen.

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in the generic formulae presented herein, which may be formulated into herbicidal compositions and applied as herein illustrated are:

- 5 methyl *m*-[(cyclopropylcarbamoyl)oxy] carbanilate
- ethyl *m*-[(*tert*-butylcarbamoyl)oxy] carbanilate
- cyclopropyl *m*-[(isopropylcarbamoyl)oxy] carbanilate
- 10 propyl *m*-[(*tert*-butylcarbamoyl)oxy] carbanilate
- butyl *m*-[(*tert*-butylcarbamoyl)oxy] carbanilate
- methyl *m*-[(neopentylcarbamoyl)oxy] carbanilate
- 15 methyl *m*-[(*tert*-butylcarbamoyl)oxy] - *N*-methylcarbanilate
- methyl *m*-[(piperidinocarbonyl)oxy] carbanilate
- 20 methyl *m*-[(*tert*-butylmethylcarbamoyl)oxy] carbanilate
- ethyl *m*-[(ethylisopropylcarbamoyl)oxy] carbanilate
- S*-methyl *m*-[(*tert*-butylcarbamoyl)oxy] thiocarbanilate
- 25 methyl *N*-ethyl - *m*-[(methylcarbamoyl)oxy] carbanilate
- S*-methyl *m*-[(isopropylcarbamoyl)oxy] thiocarbanilate
- 30 ethyl *m*-[[2-methylallyl]carbamoyl]oxy] carbanilate

It is clear that the classes of *m*-(carbamoyl-oxy)-carbanilate esters described and illustrated herein are characterized by herbicidal activity, and that the degree of this activity varies among specific compounds within these classes and to some extent among the species of plant to which these compounds may be applied. Thus, selection of a specific herbicidal compound to control undesirable plant species without injury to a desired crop species may readily be made.

The active herbicidal compounds of this invention may be formulated and/or applied with insecticides, fungicides, nematocides, plant growth regulators, fertilizers, and other agricultural chemicals and may be used as effective soil sterilants as well as in herbicidal applications. In applying an active compound of this invention, whether formulated alone or with other agricultural chemicals, an effective amount and concentration of the *m*-[(*N*-substituted-carbamoyl)oxy] carbanilate ester is of course employed.

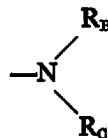
55 WHAT WE CLAIM IS:—

1. Herbicidal *m*- (carbamoyloxy) carbanilates of the formula:—

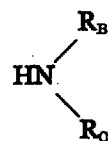


wherein R_A is the radical of an alcohol or phenol of the formula R_AOH ,

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is the radical of a primary or secondary amine of the formula:—



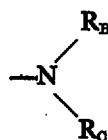
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is the radical of a *m*-aminophenol of the formula:—



and X is oxygen or sulfur with the proviso that R_A is not a methyl group when

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is a methylamino group and X is oxygen.

2. Compounds as claimed in claim 1 in which R_A is an aliphatic hydrocarbon radical.

3. Compounds as claimed in any preceding claim in which R_A , R_B , R_O and R_D contain only carbon and hydrogen.

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4. Compounds as claimed in any preceding claim in which R_B is a hydrocarbon radical and R_O is hydrogen or a hydrocarbon radical.

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5. Compounds as claimed in any preceding claim in which R_D is a hydrogen atom or a methyl group.

6. Compounds as claimed in claim 4 or 5 in which the sum of the lengths of the longest straight chain, or single carbon, of the R_B substituent and the longest straight chain, or single carbon, of any R_O substituent is at most four carbon atoms.

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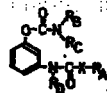
7. Compounds as claimed in any of claims 4 to 6 in which R_A is an aliphatic hydrocarbon radical of one to four carbon atoms and X is oxygen.

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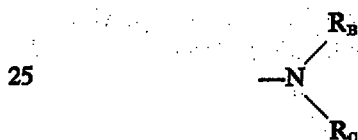
8. Compounds as claimed in claim 7 in which R_A is alkyl of one to four carbons and X is oxygen.

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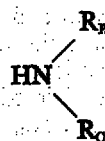
9. Compounds as claimed in any of claims 4 to 6 in which R_A is an aliphatic hydrocarbon radical of less than three carbon atoms and X is sulfur.
10. Compounds as claimed in claim 9 in which R_A is alkyl of less than three carbon atoms and X is sulfur.
11. Compounds as claimed in any preceding claim in which R_A is a methyl radical.
12. Methyl *m* - [(isopropylcarbamoyl)oxy] carbanilate.
13. Methyl *m* - [(*tert* - butylcarbamoyl)oxy] carbanilate.
14. Herbicidal *m* - (carbamoyloxy) carbanilates as claimed in claim 1 substantially as hereinbefore described with reference to the foregoing Examples.
15. Herbicidal compositions comprising as an essential active ingredient a herbicidally effective amount of a *m*-(carbamoyloxy) carbanilate of the formula,



wherein R_A is the radical of an alcohol or phenol of the formula R_AOH ,



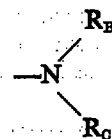
is the radical of a primary or secondary amine of the formula:—



- 30 is the radical of a *m*-aminophenol of the formula:—



and X is oxygen or sulfur with the proviso that R_A is not a methyl group when



is a methylamino group and X is oxygen, in admixture with adjuvants and carriers normally employed for agricultural dispersion.

16. Herbicidal compositions as claimed in claim 15 in which R_A , R_B , R_C and R_D contain only carbon and hydrogen.

17. Herbicidal compositions as claimed in claim 15 in which R_B is a hydrocarbon radical, and R_C is hydrogen or a hydrocarbon radical.

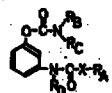
18. Herbicidal compositions as claimed in any of claims 15 to 17 in which R_D is a hydrogen atom or a methyl group.

19. Herbicidal compositions as claimed in any of claims 15 to 18 in which the sum of the lengths of the longest straight chain or single carbon of the R_B substituent, and the longest straight chain or single carbon of any R_C substituent, is at most four carbon atoms.

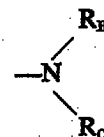
20. Herbicidal compositions as claimed in any of claims 15 to 19 in which R_A is alkyl of one to four carbon atoms and X is oxygen.

21. Herbicidal compositions as claimed in any of claims 15 to 20 in which R_A is methyl.

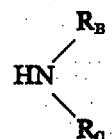
22. Method of controlling undesired plant growth which comprises applying to the locus wherein control is desired a herbicidal amount of a *m*-(carbamoyloxy) carbanilate of the formula:—



wherein R_A is the radical of an alcohol or phenol of the formula R_AOH ,

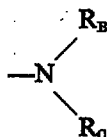


is the radical of a primary or secondary amine of the formula:—





is the X is oxygen or sulfur with the proviso that R_A is not a methyl group when



5 is a methylamino group and X is oxygen.
23. Method as claimed in claim 22 in which R_A , R_B , R_O and R_D contain only carbon and hydrogen.

24. Method as claimed in claim 22 in which R_B is a hydrocarbon radical, and R_O is hydrogen or a hydrocarbon radical.

25. Method as claimed in any of claims 22 to 24 in which R_D is a hydrogen atom or a methyl group.

15 26. Method as claimed in any of claims 22 to 25 in which the sum of the lengths of the longest straight chain or single carbon of the R_B substituent, and the longest straight chain or single carbon of any R_O substituent, is at most four carbon atoms.

20 27. Method as claimed in any of claims 22 to 26 in which R_A is alkyl of one to four carbon atoms and X is oxygen.

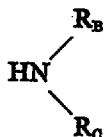
28. Method as claimed in any of claims 25 22 to 27 in which R_A is methyl.

29. Process for the production of herbicidal *m*-(carbamoyloxy) carbanilates of the formula given in claim 1 which comprises reacting a compound of the formula:—

30

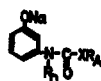


with an amine of the formula:—

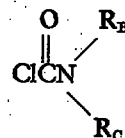


in which R_A , R_B , R_O , R_D and X are as defined in claim 1.

35 30. Process for the production of herbicidal *m*-(carbamoyloxy) carbanilates of the formula given in claim 1 which comprises reacting a compound of the formula:—

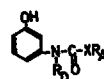


with a compound of the formula:—



in which R_A , R_B , R_O , R_D and X are as defined in claim 1.

31. Process for the production of herbicidal *m*-(carbamoyloxy) carbanilates of the formula given in claim 1 but where R_O is hydrogen which comprises reacting a compound of the formula:—



with an isocyanate of the formula:—



in which R_A , R_B , R_D and X are as defined in claim 1.

32. Process as claimed in claim 31 in which R_A , R_B and R_D contain only carbon and hydrogen.

33. Process for the production of herbicidal *m*-(carbamoyloxy) carbanilates of the formula given in claim 1 which comprises reacting a compound of the formula:—



with a compound of the formula:—



in which R_A , R_B , R_O , R_D and X are as defined in claim 1.

34. Process as claimed in any of claims 29, 30, and 33 in which R_A , R_B , R_O and R_D contain only carbon and hydrogen.

35. Process as claimed in any of claims 29, 30, and 33 in which R_B is a hydrocarbon radical, and R_O is hydrogen or a hydrocarbon radical.

36. Process as claimed in any of claims 30 to 35 in which R_D is a hydrogen atom or a methyl group.

37. Process as claimed in any of claims 29, 30, 33 to 36 in which the sum of the lengths of the longest straight chain or single carbon of the R_B substituent, and the longest straight chain or single carbon of any R_O substituent, is at most four carbon atoms.

38. Process as claimed in any of claims



30 to 37 in which R_A is alkyl of one to four carbon atoms and X is oxygen.

39. Process as claimed in any of claims 30 to 38 in which R_A is methyl.

5 40. Herbicidal compositions comprising a herbicidally effective amount of a *m*-carbamoyloxy) carbanilate in admixture with adjuvants and carriers substantially as hereinbefore described.

10 41. Method of controlling undesired plant growth substantially as hereinbefore described.

42. Process for the preparation of herbi-

cidal *m*-(carbamoyloxy) carbanilates substantially as hereinbefore described with reference to the foregoing Examples.

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