United States Patent [19]

Pallos

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[54] **HALOGENATED ESTERS AS HERBICIDE ANTIDOTES**

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[52] **U.S. Cl.** **71/100;** 71/79; 71/106

[51] **Int. Cl.** **A01n 9/12**

[58] **Field of Search** ..... 71/79, DIG. 1, 100, 106

[56] **References Cited**

UNITED STATES PATENTS

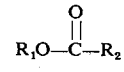
2,913,327	11/1959	Tilles et al.	71/100
3,095,299	6/1963	Luckenbaugh	71/100
3,131,509	5/1964	Hoffman	71/79
3,564,768	2/1971	Hoffman	71/79
3,719,466	3/1973	Ahle	71/88

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Attorney, Agent, or Firm—Harry A. Pacini; Daniel C. Block; Edwin H. Baker

[57] **ABSTRACT**

Herbicidal compositions comprising an active herbicidal compound and antidote therefor and the methods of use; the antidote compounds correspond to the halogenated esters having the formula



wherein R_1 is lower haloalkyl, alkynyl, alkenyl and N,N-dialkenylaminoalkyl and R_2 is lower haloalkyl.

11 Claims, No Drawings

HALOGENATED ESTERS AS HERBICIDE ANTIDOTES

BACKGROUND OF THE INVENTION

Among the many herbicidal compounds commercially available, the thiocarbamates alone or admixed with other herbicides, such as the triazines, have reached a relatively high degree of commercial success. These herbicides are immediately toxic to a large number of weed pests at different concentrations varying with the resistance of the weed pests. Some examples of these compounds are described and claimed in U.S. Pat. Nos. 2,913,327, 3,037,853, 3,175,897, 3,185,720, **3,198,786** and 3,582,314.

It has been found in practice that the use of these thiocarbamates as herbicides on crops sometimes causes serious injuries to the crop plant. When used in the recommended amounts in the soil to control many broadleaf weeds and grasses, serious malformation and stunting of the crop plants result. This abnormal growth in the crop plants results in loss of crop yield. Previous attempts to overcome this problem involves the treatment of the crop seed with certain antagonistic agents prior to planting, see U.S. Pat. Nos. 3,131,509 and 3,564,768. These antagonistic agents have not been notably successful. The aforementioned patent specifically exemplifies the treatment of seeds employing compounds of a different chemical class not suggestive of the present invention.

DESCRIPTION OF THE INVENTION

It has been discovered that plants can be protected against injury by various herbicides, for example, the thiocarbamate-type herbicides, alone or mixed with other herbicidal compounds and/or the tolerance of the plants can be substantially increased to the active compounds of the above-noted U.S. patents by adding to the soil an antidote compound corresponding to the following formula

$$R_1O-\overset{\overset{O}{\|}}{C}-R_2$$

wherein R_1 is lower haloalkyl, alkynyl, alkenyl and N,N-dialkenylaminoalkyl and R_2 is lower haloalkyl.

In the description of the halogenated esters as compounds useful in the herbicidal antidote method of this invention, the following embodiments are intended for the various groups: The term halo preferably refers to fluoro, chloro and bromo substitutions in mono, di, tri, tetra and per substitution. Halo also is intended to relate to mixed halogen substitution, such as in dichloromonofluoromethyl and the like. Alkynyl preferably includes those members having at least one carbon-to-carbon triple bond and from 3 to 6 carbon atoms, inclusive. The term alkenyl preferably includes those members having at least one carbon-to-carbon double bond and from 3 to 6 carbon atoms, inclusive. In the term N,N-dialkenylaminoalkyl, the alkyl moiety preferably includes those members having 1 to 4 carbon atoms, inclusive, alkenyl is as defined hereinabove. The term lower haloalkyl preferably has halo-substitution as denoted above and lower alkyl moiety having from 1 to 4 carbon atoms, inclusive, for example, monochloromethyl, monobromomethyl, monofluoromethyl, dichloromethyl, dibromomethyl, 1,1-dichloroethyl, 1,2-dichloroethyl, 1,1,1-trichloroethyl, dichloromonofluoromethyl, 1-chlorobutyl, 1-fluorobutyl, 1-bromobutyl, 1,4-dichlorobutyl and the like.

As an alternative mode of action, the compounds of this invention may interfere with the normal herbicidal action of the thiocarbamate-type and other herbicides to render them selective in their action. Whichever mode of action is present, the corresponding beneficial and desirable effect is the continued herbicidal effect of the thiocarbamate with the accompanying decreased herbicidal effect on desired crop species. This advantage and utility will become more apparent hereinafter.

Therefore, the terms herbicide antidote or antidotal amount, is meant to describe that effect which tends to counteract the normal injurious herbicidal response that the herbicide might otherwise produce. Whether it is to be termed a remedy, interferant, protectant, or the like, will depend upon the exact mode of action. The mode of action is varied, but the effect, which is desirable, is the result of the method of treating the soil in which a crop is planted. Hitherto, there have been no systems which have been satisfactory for this purpose.

The compounds of this invention represented by the above formula can be prepared by several different procedures depending upon the starting materials.

The reaction of a halogen-containing chloride with an alcohol to form an ester is well known. The same general method is used in the preparation of the compounds of this invention; however, certain modifications of the reaction have been made to simplify the procedure and to insure in most instances high yields. The modifications include the use of a solvent such as benzene or methylene chloride; the use of a hydrogen chloride acid acceptor such as triethylamine. After completion of the reaction, the product is conveniently isolated by conventional techniques.

The following examples, which are illustrative of the compounds useful in the instant invention, should not be construed as limiting examples, variations and modifications thereof will be apparent to one having ordinary skill in this art.

EXAMPLE I

Preparation of 2-bromoethyl dichloroacetate

Dichloroacetyl chloride (7.4 g., 0.05 mole) was dissolved in 200 ml. benzene, 2-bromoethanol (6.2 g., 0.05 mole) was added. Triethylamine (5.1 g., 0.05 mole) in 10 ml. benzene was slowly added. The temperature was kept below 30°C. After the addition was complete, the resulting solution was refluxed for one hour. The reaction mixture was washed with water, dried over magnesium sulfate, filtered and the solvent removed under vacuum. There was obtained 10.6 g. of the title compound, $n_D^{30} = 1.4972$.

EXAMPLE II

Preparation of Propargyl dichloroacetate

In a similar procedure as Example I, 2.8 g., 0.05 mole of propargyl alcohol in 40 ml. of methylene chloride was reacted with 7.4 g., 0.05 mole, of dichloroacetyl chloride in the presence of 5.2 g. triethylamine. There was obtained 5.5 g. of the title compound, $n_D^{30} = 1.4680$.

EXAMPLE III

Preparation of N,N-diallylaminoethyl dichloroacetate

In a similar method as described in Example I, 3.5 g., 0.025 mole, of N,N-diallylaminoethanol in 26 ml. methylene chloride was reacted with 3.7 g., 0.025 mole, of dichloroacetyl chloride in the presence of 2.6 g. triethylamine. There was obtained 3.7 g. of the title compound, $n_D^{30} = 1.4700$.

The compounds of the present invention and their preparation are more particularly illustrated by the following table. Following is a table of compounds which are prepared according to the procedures described herein. Compound numbers have been assigned to them and are used for identification throughout the balance of the specification.

TABLE I

$R_1O-\overset{\overset{O}{\|}}{C}-R_2$

COMPOUND NUMBER	R_1	R_2	m.p. °C. or n_D^{30}
1	CH_2CH_2Br	$CHCl_2$	1.4972
2	CH_2CH_2Cl	$CHCl_2$	1.4780
3	$CH_2C \equiv CH$	$CHCl_2$	1.4680
4	$CH_2O-C\equiv CCH_3$	$CHCl_2$	1.4730
5	$CH_2CH_2N(CH_2CH=CH_2)_2$	$CHCl_2$	1.4700
6	$CH_2CH=CH_2$	$CHCl_2$	1.4580

The compounds of this invention were employed in effective herbicidal antidote compositions comprising thiocarbamates in combination with antidote compounds described hereinabove.

Corn Seed Treatment Test

Small flats were filled with Felton loamy sand soil. Soil incorporated herbicides were applied at this time. The soil from each flat was placed into a 5-gallon cement mixer where the soil was mixed as the herbicides were applied using a predetermined amount of a stock solution containing 936 mg. of 75.5% active ingredient to 100 ml. of water. One ml. of stock solution was applied to the soil in a volumetric pipet for each pound of herbicide desired. One ml. of stock solution contained 7 mg. of herbicide which equals one pound per acre when applied to the soil in the flats. After the herbicide incorporation, the soil was placed back into the flats.

Flats of herbicide-treated and untreated soil were then ready to be planted. A pint sample of soil was removed from each flat and placed next to each flat for later use in covering up the seeds. The soil was leveled and rows one-half inch deep were made for planting seeds. Alternating rows of treated and untreated crop seeds were sown. In each test, six PAG 344T or DeKalb XL374 field corn seeds were planted in each row. Rows were approximately 1½ inches apart in the flat. Seeds were treated by placing 50 mg. of the antidote compound with 10 grams of corn seed (0.5% w/w) in a suitable container and shaking them until the seeds were uniformly covered with the compound. Antidote compounds were also applied as liquid slurries and powders or dusts. In some cases, acetone was used to dissolve powdered or solid compounds so they could be more effectively applied to the seeds.

After the flats were seeded, they were covered with the 1 pint of soil which had been removed just prior to planting. Flats were placed on greenhouse benches where temperatures ranged from 70°–90°F. Flats were watered by sprinkling as needed to assure good plant growth. Percent control ratings were taken 2, 3 and 4 weeks after the treatments were applied.

In each test, the herbicide was applied alone, in combination with the seed protectant, and the seed protectant was applied alone to check for phytotoxicity. The untreated adjacent row was employed to observe any beneficial lateral movement of the antidote compound through the soil. The degree of the effect was noted by comparison with the control. The results of these tests are tabulated in Table II.

TABLE II

Percent Injury to Corn from EPTC*
Seed Treatment Test

COMPOUND NUMBER	Percent Injury, 2 Weeks Treated Seed (0.5% w/w)	Untreated Seed Adjacent Row
1	0	98
2	60	88
3	20	50
4	30 (4 weeks)	65
5	30	65
6	30	65

*EPTC = S-ethyl dipropylthiocarbamate 6E: 6 lb/A pre-plant incorporated

The antidote compounds and compositions of the present invention can be used in any convenient form. Thus, the antidote compounds can be formulated into emulsifiable liquids, emulsifiable concentrates, liquid, wettable powder, powders, granular or any other convenient form. In its preferred form, a non-phytotoxic quantity of an herbicidal antidote compound is admixed with a selected herbicide and incorporated into the soil prior to or after planting the seed. It is to be understood, however, that the herbicides can be incorporated into the soil and thereafter the antidote compound can be incorporated into the soil. Moreover, the crop seed itself can be treated with a non-phytotoxic quantity of the compound and planted into the soil which has been treated with herbicides, or untreated with the herbicide and subsequently treated with the herbicide. The addition of the antidote compound does not affect the herbicidal activity of the herbicides.

The amount of antidote compound present can range between about 0.001 to about 15 parts by weight of antidote compound described herein per each part by weight of herbicide. The exact amount of antidote compound will usually be determined on economic ratios for the most effective amount usable. It is understood that a non-phytotoxic quantity of antidote compound will be employed in the herbicidal compositions described herein.

The herbicides indicated in the tables and elsewhere are used at rates which produce effective control of undesirable vegetation. The rates are within the recommended amounts set forth by the supplier. Therefore, the weed control in each instance is commercially acceptable within the desired or recommended amount.

It is clear that the classes of herbicidal agents described and illustrated herein are characterized as effective herbicides exhibiting such activity. The degree of this herbicidal activity varies among specific com-

pounds and among combinations of specific compounds within the classes. Similarly, the degree of activity to some extent varies among the species of plants to which a specific herbicidal compound or combination may be applied. Thus, selection of a specific herbicidal compound or combination to control undesirable plant species readily may be made. Within the present invention are prevention of injury to a desired crop species in the presence of a specific compound or combination may be achieved. The beneficial plant species which can be protected by this method is not intended to be limited by the specific crops employed in the examples.

The herbicidal compounds employed in the utility of this invention are active herbicides of a general type. That is, the members of the classes are herbicidally effective against a wide range of plant species with some degree of discrimination between desirable and undesirable species. The method of controlling vegetation comprises applying an herbicidally effective amount of the hereindescribed herbicidal compounds to the area or plant locus where control is desired. The compositions as set forth in this invention include those wherein the preferred active herbicidal compound is selected from S-ethyl dipropylthiocarbamate, S-ethyl diisobutyl thiocarbamate, S-propyl dipropylthiocarbamate, S-2,3,3-trichloroallyl-diisopropyl thiocarbamate, S-ethyl cyclohexyl ethyl thiocarbamate, 2-chloro-2',6''-diethyl-N-(methoxymethyl)acetanilide, S-ethyl hexahydro-1H-azepine-1-carbothioate, 2-chloro-N-isopropylacetanilide, N,N-diallyl-2-chloroacetamide, S-4-chlorobenzyl diethyl thiocarbamate, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, 2-chloro-4,6-bis(ethylamino)-s-triazine, 2(4-chloro-6-ethylamine-s-triazine-2-yl-amino)-2-methylpropionitrile, 2-chloro-4-cyclopropylamino-6-isopropylamino-s-triazine, 2,4-dichlorophenoxyacetic acid, its esters and salts, and 3-(3,4-dichlorophenyl)-1,1-dimethylurea and combinations thereof.

An herbicide as used herein means a compound which controls or modifies the growth of vegetation or plants. Such controlling or modifying effects include all deviations from natural development; for example, killing, retardation, defoliation, desiccation, regulation, stunting, tillering, stimulation, dwarfing and the like. By "plants" it is meant germinant seeds, emerging seedlings, and established vegetation, including the roots and above-ground portions.

What is claimed is:

1. The method of reducing injury to corn crops injured by thiocarbamate herbicides comprising applying to the corn seeds prior to planting a nonphytotoxic antidotally effective amount of a compound corresponding to the formula

$$R_1OCR_2$$

wherein R_1 is lower haloalkyl, alkynyl, alkenyl and N,N-dialkenylaminoalkyl and R_2 is lower haloalkyl.

2. The method according to claim **1** in which R_1 is lower haloalkyl and R_2 is lower haloalkyl.

3. The method according to claim **2** in which R_1 is 2-bromoethyl and R_2 is dichloromethyl.

4. The method according to claim **2** in which R_1 is 2-chloroethyl and R_2 is dichloromethyl.

5. The method according to claim **1** in which R_1 is alkynyl and R_2 is lower haloalkyl.

6. The method according to claim **5** in which R_1 is 2-propynyl and R_2 is dichloromethyl.

7. The method according to claim **5** in which R_1 is 2-butynyl and R_2 is dichloromethyl.

8. The method according to claim **1** in which R_1 is alkenyl and R_2 is lower haloalkyl.

9. The method according to claim **8** in which R_1 is 2-propenyl and R_2 is dichloromethyl.

10. The method according to claim **1** in which R_1 is N,N-dialkenylaminoalkyl and R_2 is lower haloalkyl.

11. The method according to claim **10** in which R_1 is N,N-dialkylaminoethyl and R_2 is dichloromethyl.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,893,838

DATED : July 8, 1975

INVENTOR(S) : Ferenc M. Pallos

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 3, Table I, under the column "R_1", the entry for Compound No. 3 should read --- $CH_2C{\equiv}CH$ ---.

In Column 3, Table I, under the column "R_1", the entry for Compound No. 4 should read --- $CH_2C{\equiv}CCH_3$ ---.

Signed and Sealed this

Twenty-eighth Day of December 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks