

1010.742



PATENT SPECIFICATION

NO DRAWINGS

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Application made in United States of America (No. 78341) on Dec. 27, 1960.

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Int. Cl.:—A 01 n 19/02



COMPLETE SPECIFICATION

Herbicidal Compositions containing Uracil Derivatives

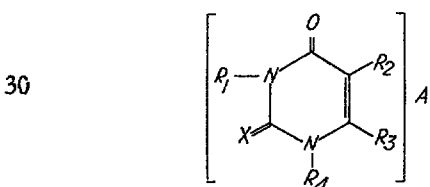
Substituents

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, 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 relates to novel herbicidal compositions containing uracil derivatives and is an improvement in or modification of the invention described in Specification No. 968,661.

Our Specification No. 968,661 discloses that certain 3-substituted uracils of defined formula have herbicidal activity. The present invention is concerned with a group of closely related acid addition compounds of 3-substituted uracils which also have herbicidal activity. Other 3-substituted uracils having herbicidal activity are disclosed in our Specifications Nos. 968,662, 968,663, 968,664, 968,665 and 968,666.

According to the invention, there are provided herbicidal compositions containing an adjuvant suitable for use in herbicidal compositions and a compound of the formula



I

wherein:

R₁ has a molecular weight of 15—250 and is a substituted or unsubstituted alkyl, cycloalkyl, cycloalkyl alkyl, alkenyl, cycloalkenyl, cycloalkenyl alkyl, alkynyl,

aralkyl or aryl radical in which any substituents are fluorine, bromine or chlorine atoms or nitro, cyano, mercapto, hydroxy, alkyl or alkoxy radicals;

R₂ has a molecular weight of up to 250 and is a hydrogen or halogen atom, a nitro, thiocyno or alkylthiol radical or a substituted or unsubstituted alkyl, alkoxy or alkenyl radical in which any substituents are fluorine, bromine or chlorine atoms or cyano, mercapto or hydroxy radicals;

R₃ has a molecular weight of up to 200 and is a hydrogen, chlorine or bromine atom or an alkyl, haloalkyl or alkoxy radical; or R₂ and R₃ together form a divalent alkylene bridge of formula (CH₂)_n where n is 3, 4 or 5;

R₄ is a hydrogen atom or an alkyl group containing from 1 to 5 carbon atoms;

X is oxygen or sulphur; and

A is boron trifluoride or an acid having an ionization constant in water at 25°C. greater than 2 × 10⁻³ and is a halogenated aliphatic acid containing 2 to 5 carbon atoms, a halogenated benzoic acid, a halogenated phenyl acetic acid, a halogenated phenoxy acetic acid, an organic sulphonic acid, an organic phosphonic acid, or an inorganic phosphoric acid.

The term adjuvant is used above to include materials known in the art as modifiers and diluents.

The preferred radicals in the R₁ position are acyclic alkyl radicals of from 1 to 10 carbon atoms, cycloalkyl radicals of from 5 to 8 carbon atoms, cycloalkyl alkyl and cycloalkenyl alkyl groups, and phenyl, halophenyl, nitrophenyl, alkylphenyl, and alkoxyphenyl radicals. These preferred radicals may be substituted or unsubstituted.

The radicals preferred in the R₂ position are hydrogen, halogen, alkyl containing from 1 to 4 carbon atoms, and substituted alkyl containing from 1 to 4 carbon atoms.

[Price 4s. 6d.]

Hydrogen and alkyl radicals containing from 1 to 4 carbon atoms are preferred in the R₃ position.

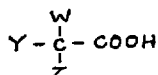
Hydrogen is preferred in the R₄ position and oxygen is preferred as X.

The uracil ring is numbered clockwise from the nitrogen atom carrying the R₄ group. Thus R₁, R₂, R₃ and R₄ are in the 3, 5, 6 and 1 positions respectively.

These uracil addition compounds are new compounds and are claimed as such in our Application No. (1,010,743) 29040/65, where their preparation is described in detail. They have herbicidal activity and generally show good oil solubility, which is advantageous for their use as herbicides.

The acid A may for example be 2,3,5-trichlorobenzoic acid, 2,3,6 - trichlorobenzoic acid, 2,3,5,6 - tetrachlorobenzoic acid, 2,3,5,6-triiodobenzoic acid, 2 - methoxy - 3,6 - dichlorobenzoic acid, 2 - methoxy - 3,5,6 - trichlorobenzoic acid, 2 - methyl - 3,6 - dichlorobenzoic acid, 2,5 - dichloro - 3 - aminobenzoic acid, 2,5 - dichloro - 3 - nitrobenzoic acid, 2,3,6 - trichlorophenylacetic acid, 2,3,5,6-tetrachlorophenylacetic acid, 2 - methoxy - 3,6-dichlorophenylacetic acid, 2,4 - dichlorophenoxylacetic acid, 2,4,5 - trichlorophenoxylacetic acid, phosphoric acid, methane phosphonic acid and phenylphosphonic acid.

The addition compounds of α -halogenated aliphatic acids form a preferred group because they generally have good grass-killing power and are easy to prepare. These acids can be represented by the formula:



wherein W is halogen; Y is halogen, or an alkyl or haloalkyl radical preferably containing 1 to 3 carbon atoms; and Z is halogen or alkyl.

Illustrative of these acids are: trichloroacetic acid, tribromoacetic acid, trifluoroacetic acid, α,α -dichloropropionic acid, α,α -dibromopropionic acid, α,α,β -trichloropropionic acid, α,α,β -trifluoropropionic acid, α,α -dichlorobutyric acid, α,β -dichloroisobutyric acid, α,β,β -trichloroisobutyric acid, and α,α -dichlorovaleric acid.

Also preferred because of their generally high herbicidal activity as foliage sprays are addition compounds with acids of the formula RSO₃H, where R is an aliphatic hydrocarbon radical, an aryl hydrocarbon radical, or a substituted aryl hydrocarbon radical, all preferably containing more than 5 carbon atoms. Illustrative of these acids are: methanesulphonic acid, ethanesulphonic acid, dodecylsulphonic acid, benzenesulphonic acid, *p*-tolylsulphonic acid, dodecylbenzenesulphonic acid, 2,4,6-trichloro-

benzenesulphonic acid and naphthalene- β -sulphonic acid.

It should be understood that the exact formulae of these uracil addition compounds are not known. On the basis of the best available information, it is believed that the elements have the configuration shown in formula ~~X~~, but it is intended that this invention embrace these addition compounds whatever their structure, and formula ~~X~~ should therefore not be construed as limiting.

Some of the uracil addition compounds are especially useful in controlling the growth of weeds on uncultivated areas. Thus in suitable circumstances some of the uracils can be used as general-purpose weed killers, as soil sterilants, and in soil-foliage applications; for the latter use rates of 5 to 35 pounds of active ingredient per acre are generally satisfactory. For example, the growth of weeds may be controlled on industrial sites, railroad ballast and agricultural areas on which no crop is growing.

In suitable cases the uracil addition compounds can be used to obtain selective control of weeds in the presence of crops. For such use pre-emergence application is usually preferred, in which case rates of 0.25 to 5, preferably 0.5 to 4, pounds of active ingredient per acre are usually satisfactory. The uracil addition salts can also be used in some cases for post-emergence weed control.

Among the weeds whose growth can be controlled are annual and perennial broadleaf weeds and grasses. When applied as a pre-emergence treatment, the uracil addition compounds will frequently control one or more germinating broadleaf weeds, e.g. pigweed, lamb's quarter, mustard, chickweed, and ragweed; and/or one or more grass weeds, e.g. crabgrass, watergrass, giant foxtail, and seedling Johnson grass. In suitable cases one or more of these weeds can be controlled in the presence of such crops as asparagus, sugar cane, gladiolus, potatoes, pineapple, safflower, sugar beet and flax.

In soil-foliage applications, the compounds can frequently be used to control existing mixed annual and perennial vegetation composed of one or more broadleaf and grass weeds such as crabgrass, foxtail, watergrass, quackgrass, bermuda grass, Johnson grass, dallis grass, vasey grass, brome grass, ragweed, cocklebur, pigweed, lamb's quarter, mare's tail, wild carrot, plantain, and goldenrod.

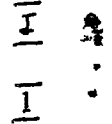
The concentration at which the acid addition compounds are to be used as herbicides will naturally vary according to the result desired, the type of vegetation, the formulation used, the mode of application, weather conditions, foliage density, and other similar factors. Since so many variables play a role, it is not possible to indicate a concentration suitable for all situations. The determination of the optimum concentration to be used in any particular



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application can easily be made by one skilled in the art.

These compounds can be formulated for use as herbicides by mixing them, in herbicidally effective amounts, with adjuvants suitable for use in herbicidal compositions. Suitable adjuvants and procedures for formulating herbicidal compositions with them are disclosed in U.S. Patents 2,782,112; 2,801,911; 2,843,470; 2,849,306; 2,854,375; and 2,895,817. By substituting the uracil addition compounds, in the proper proportions, for the active ingredients disclosed in the patents, one can formulate effective herbicidal compositions. The portions of these patents and the patents cited therein which disclose adjuvants and herbicidal formulations are hereby incorporated by reference.

The uracil addition compounds have high oil solubility and can therefore be advantageously formulated in oils. Since the compounds are prepared in a hydrocarbon solvent, it is not necessary in preparing oil formulations to isolate the compounds from the reaction medium. The reaction solution can simply be mixed with an additional hydrophobic liquid diluent e.g. xylene, alkylated naphthalene, or an aromatic herbicidal oil.

Oils of petroleum origin can also be used. Aromatic hydrocarbons having boiling points of from 125°C. to 400°C. are preferred. Hydrocarbon oils having lower boiling points should not be used because they volatilize undesirably when sprayed from a nozzle and are inflammable.

The herbicidal compositions are generally formulated so that they contain from 0.5% to 95% by weight of the uracil addition compound. The exact proportion will naturally vary with the compound, the intended use, and the degree of weed control desired. The herbicidal compositions may also contain other compounds having herbicidal activity.

The following Examples illustrate the invention.

EXAMPLE 1—Oil Solution

An oil solution is prepared by mixing the following components until the solution is homogeneous:

50	3 - isopropyl - 5 - bromo - 6-methyluracil 1/1 addition compound with dodecylbenzene sulphonate	40% by weight
	Xylene	53% by weight
55	Dodecylbenzene sulphonate	7% by weight

This formulation is applied at the rate of 15 to 25 pounds of active ingredient in 60 gallons of diesel oil per acre, to railroad ballast where it is difficult to control weeds with most commercial herbicides. Fast-acting, long-lasting weed control of such annual and perennial weeds as crabgrass, mustard, Johnson grass, bermuda grass, orchard grass, blue grass, and pigweed is obtained.

EXAMPLE 2—Wettable Powder

The following wettable powder is prepared by blending and micropulverising the ingredients until most particles are below 50 microns in size, and then reblending:

3 - isopropyl - 5 - chloro - 6-methyluracil 1/1 addition compound with dodecylbenzene sulphonate	25% by weight	
Partially desulphonated sodium lignin sulphonate	1% by weight	75
Calcined, non-swelling montmorillonoid-type clay (Pikes Peak Clay)	74% by weight	

This composition is applied to emerged weed seedlings in sugar cane or asparagus. It is applied at 0.75 to 2.0 pounds of active ingredient per acre, dispersed in 40 gallons of water. Excellent control of pigweed, mustard, chickweed, lamb's quarter, crabgrass, watergrass, foxtail, Johnson grass seedlings, and wild oats is obtained.

EXAMPLE 3—Oil-dispersible Powder

3 - isopropyl - 5 - bromo - 6-methyluracil 1/1 addition compound with trichloroacetic acid	80% by weight	90
Blend of oil-soluble sulphonates and polyoxyethylene ethers	3% by weight	
Attapulgate clay	17% by weight	95

These ingredients are mixed, blended, and ground in a hammer mill, using care to maintain a dry mix.

This formulation is applied at a rate of 20 pounds of active ingredient per acre in 70 gallons of Lion Herbicidal Oil No. 6 for control of annual and perennial broadleaf and grass weeds growing on an industrial site. Excellent control of crabgrass, nutsedge, bromsedge, dallis grass, vasey grass, Johnson grass, pigweed, goldenrod, and evening primrose is obtained.

EXAMPLE 4—Oil Solution

3 - cyclohexyl - 1,6 - dimethyl - 5 - bromouracil 1/1 addition compound with α,α,β -trichloropropionic acid	20% by weight	110
α,α,β -trichloropropionic acid	3% by weight	
Xylene	77% by weight	

These ingredients are thoroughly mixed to form a homogeneous solution. This solution is diluted with 80 gallons of Lion Herbicidal Oil No. 6 and applied at 15 pounds of active ingredient per acre to give excellent control of annual morning glory, yarrow, crabgrass, quackgrass, oak and maple seedling, wild carrot, and ragweed growing along railroad rights-of-way.

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising an adjuvant suitable for use in herbicidal compositions and at least one compound of the formula:



application can easily be made by one skilled in the art.

These compounds can be formulated for use as herbicides by mixing them, in herbicidally effective amounts, with adjuvants suitable for use in herbicidal compositions. Suitable adjuvants and procedures for formulating herbicidal compositions with them are disclosed in U.S. Patents 2,782,112; 2,801,911; 2,843,470; 2,849,306; 2,854,375; and 2,895,817. By substituting the uracil addition compounds, in the proper proportions, for the active ingredients disclosed in the patents, one can formulate effective herbicidal compositions. The portions of these patents and the patents cited therein which disclose adjuvants and herbicidal formulations are hereby incorporated by reference.

The uracil addition compounds have high oil solubility and can therefore be advantageously formulated in oils. Since the compounds are prepared in a hydrocarbon solvent, it is not necessary in preparing oil formulations to isolate the compounds from the reaction medium. The reaction solution can simply be mixed with an additional hydrophobic liquid diluent e.g. xylene, alkylated naphthalene, or an aromatic herbicidal oil.

Oils of petroleum origin can also be used. Aromatic hydrocarbons having boiling points of from 125°C. to 400°C. are preferred. Hydrocarbon oils having lower boiling points should not be used because they volatilize undesirably when sprayed from a nozzle and are inflammable.

The herbicidal compositions are generally formulated so that they contain from 0.5% to 95% by weight of the uracil addition compound. The exact proportion will naturally vary with the compound, the intended use, and the degree of weed control desired. The herbicidal compositions may also contain other compounds having herbicidal activity.

The following Examples illustrate the invention.

EXAMPLE 1—Oil Solution

An oil solution is prepared by mixing the following components until the solution is homogeneous:

50 3 - isopropyl - 5 - bromo - 6-methyluracil 1/1 addition compound with dodecylbenzene sulphonic acid 40% by weight
Xylene 53% by weight
55 Dodecylbenzene sulphonic acid 7% by weight

This formulation is applied at the rate of 15 to 25 pounds of active ingredient in 60 gallons of diesel oil per acre, to railroad ballast where it is difficult to control weeds with most commercial herbicides. Fast-acting, long-lasting weed control of such annual and perennial weeds as crabgrass, mustard, Johnson grass, bermuda grass, orchard grass, blue grass, and pigweed is obtained.

EXAMPLE 2—Wettable Powder

The following wettable powder is prepared by blending and micropulverising the ingredients until most particles are below 50 microns in size, and then reblending:

3 - isopropyl - 5 - chloro - 6-methyluracil 1/1 addition compound with dodecylbenzene sulphonic acid 25% by weight
Partially desulphonated sodium lignin sulphonate 1% by weight
75 Calcined, non-swelling montmorillonoid-type clay (Pikes Peak Clay) 74% by weight

This composition is applied to emerged weed seedlings in sugar cane or asparagus. It is applied at 0.75 to 2.0 pounds of active ingredient per acre, dispersed in 40 gallons of water. Excellent control of pigweed, mustard, chickweed, lamb's quarter, crabgrass, watergrass, foxtail, Johnson grass seedlings, and wild oats is obtained.

EXAMPLE 3—Oil-dispersible Powder

3 - isopropyl - 5 - bromo - 6-methyluracil 1/1 addition compound with trichloroacetic acid 80% by weight
Blend of oil-soluble sulphonates and polyoxyethylene ethers 3% by weight
Attapulgite clay 17% by weight
95

These ingredients are mixed, blended, and ground in a hammer mill, using care to maintain a dry mix.

This formulation is applied at a rate of 20 pounds of active ingredient per acre in 70 gallons of Lion Herbicidal Oil No. 6 for control of annual and perennial broadleaf and grass weeds growing on an industrial site. Excellent control of crabgrass, nutsedge, bromsedge, dallis grass, vasey grass, Johnson grass, pigweed, goldenrod, and evening primrose is obtained.

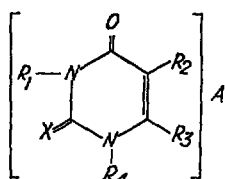
EXAMPLE 4—Oil Solution

3 - cyclohexyl - 1,6 - dimethyl - 5 - bromouracil 1/1 addition compound with α,α,β -trichloropropionic acid 20% by weight
 α,α,β -trichloropropionic acid 3% by weight
Xylene 77% by weight
110

These ingredients are thoroughly mixed to form a homogeneous solution. This solution is diluted with 80 gallons of Lion Herbicidal Oil No. 6 and applied at 15 pounds of active ingredient per acre to give excellent control of annual morning glory, yarrow, crabgrass, quackgrass, oak and maple seedling, wild carrot, and ragweed growing along railroad rights-of-way.

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising an adjuvant suitable for use in herbicidal compositions and at least one compound of the formula:



wherein:

R_1 has a molecular weight of 15—250 and is a substituted or unsubstituted alkyl, cycloalkyl, cycloalkyl alkyl, cycloalkenyl alkyl, alkenyl, cycloalkenyl, alkynyl, aralkyl or aryl radical in which any substituents are fluorine, bromine or chlorine atoms or nitro, cyano, mercapto, hydroxy, alkyl or alkoxy radicals;

R_2 has a molecular weight of up to 250 and is a hydrogen or halogen atom, a nitro, thiocyanate or alkylthiol radical or a substituted or unsubstituted alkyl, alkoxy or alkenyl radical, in which any substituents are fluorine, bromine or chlorine atoms or cyano, mercapto or hydroxy radicals;

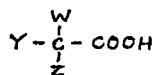
R_3 has a molecular weight of up to 200 and is a hydrogen, chlorine or bromine atom or an alkyl, haloalkyl or alkoxy radical; or R_2 and R_3 together form a divalent alkylene bridge of formula $(CH_2)_n$ where n is 3, 4 or 5;

R_4 is a hydrogen atom or an alkyl group containing from 1 to 5 carbon atoms;

X is oxygen or sulphur; and

A is boron trifluoride or an acid having an ionization constant in water at 25°C . greater than 2×10^{-5} and is a halogenated aliphatic acid containing 2 to 5 carbon atoms, a halogenated benzoic acid, a halogenated phenyl acetic acid, a halogenated phenoxy acetic acid, an organic sulphonic acid, an organic phosphonic acid or an inorganic phosphoric acid.

2. A composition according to claim 1 wherein A is an α -halogen aliphatic acid of the formula



wherein W is a halogen atom; Y is a halogen atom or an alkyl or haloalkyl radical; and Z is a halogen atom or alkyl radical.

3. A composition according to claim 2 wherein Y represents an alkyl or haloalkyl radical containing 1 to 3 carbon atoms.

4. A composition according to any one of the preceding claims, wherein R_1 is an acyclic alkyl group of 1 to 10 carbon atoms, a cycloalkyl group of 5 to 8 carbon atoms, or a phenyl, halophenyl, nitrophenyl, alkylphenyl group or alkoxyphenyl group.

5. A composition according to any one of claims 1 to 3 wherein R_1 is a cycloalkyl alkyl or cycloalkenyl alkyl radical.

6. A composition according to any one of the preceding claims wherein R_2 is a hydrogen or halogen atom, or an unsubstituted or substituted alkyl group of 1 to 4 carbon atoms.

7. A composition according to any one of the preceding claims, wherein R_3 is a hydrogen atom or an alkyl group of 1 to 4 carbon atoms.

8. A composition according to any one of the preceding claims wherein X is oxygen.

9. A composition according to claim 1 containing a compound of the said formula hereinbefore specifically mentioned.

10. A composition according to any one of the preceding claims which contains a diluent and a surface-active agent.

11. A herbicidal composition according to any one of the preceding claims containing in addition to the uracil acid addition compound, another compound having herbicidal properties.

12. A herbicidal composition according to any one of the preceding claims containing a hydrophobic organic liquid diluent.

13. A herbicidal composition according to claim 1 substantially as hereinbefore described.

14. A herbicidal composition according to claim 1 substantially as described in any one of the foregoing Examples.

15. A method of controlling the growth of weeds at a locus which comprises applying to the locus a herbicidally effective quantity of a uracil acid addition salt as defined in any one of claims 1 to 9.

16. A method according to claim 15 wherein the uracil acid addition salt is applied in the form of a composition as claimed in any one of claims 1 to 14.

17. A method according to claim 15 substantially as hereinbefore described.

18. A method according to claim 15 substantially as described in any one of the foregoing Examples.

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