

PATENT SPECIFICATION

(11) 1284511

1284511

NO DRAWINGS

- (21) Application No. 2162/71 (22) Filed 15 Jan. 1971
 (31) Convention Application No. 7 001 573 (32) Filed 16 Jan. 1970 in
 (33) France (FR)
 (45) Complete Specification published 9 Aug. 1972
 (51) International Classification C07D 85/54; A01N 9/20
 (52) Index at acceptance
 C2C 170—27X—288 200 202 215 220 226 22Y 255 25Y
 30Y 311 313 314 315 31Y 321 322 32Y 338 341
 342 345 349 34Y 351 352 601 622 626 62X 660
 669 694 714 71X 761 768 791 79Y KD KS
 LK MH



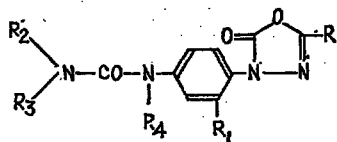
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(54) OXADIAZOLINE DERIVATIVES

(71) We, RHONE-POULENC S.A., a French Body Corporate of 22, Avenue Montaigne, Paris 8e, France, 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 new oxadiazoline derivatives, to a process for their preparation and to herbicidal compositions containing them.

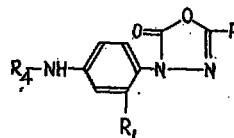
The oxadiazoline derivatives of the present invention are those of the general formula:—



I

wherein R represents an alkyl or phenyl radical, or a phenyl radical carrying at least one substituent selected from halogen atoms, and alkyl and alkoxy radicals; R₁ represents a hydrogen atom or halogen atom, or an alkyl, alkoxy, nitro or trifluoromethyl radical; R₂ represents a hydrogen atom or an alkyl, alkenyl, alkynyl, alkoxy or alkenyloxy radical; R₃ represents a hydrogen atom or an alkyl radical, and R₄ represents a hydrogen atom or an alkyl radical. In this specification the alkyl and alkoxy radicals have straight- or branched-chains containing 1 to 4 carbon atoms, and the allenyl, alkynyl and alkenyloxy radicals contain 2 to 4 carbon atoms.

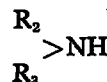
According to a feature of the invention, the oxadiazoline derivatives of general formula I are prepared, in accordance with known methods for the preparation of urea, from amines of the general formula:—



II

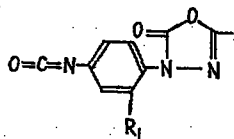
wherein R, R₁ and R₄ are as hereinbefore defined. 35

When in general formula I R₄ represents a hydrogen atom, the oxadiazoline derivatives are obtained by reaction of an amine of the general formula:— 40



III

(wherein R₂ and R₃ are as hereinbefore defined) with an isocyanate of the general formula:—



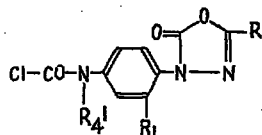
IV

wherein R and R₁ are as hereinbefore defined. 45
 The reaction is generally carried out in an inert organic solvent, for example benzene, at a temperature between 0° and 50°C. It is also possible to add an aqueous solution of the amine of general formula III to a benzene solution of the isocyanate of general formula IV, with stirring, and at a temperature between 0° and 50°C. 50

The isocyanates of formula IV can be pre-

pared by reaction of phosgene with an amine of general formula II, wherein R_1 represents a hydrogen atom.

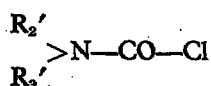
- 5 When in general formula I R_1 represents an alkyl radical, the oxadiazoline derivatives are obtained by reaction of an amine of general formula III with a compound of the general formula:—



V

- 10 wherein R and R_1 are as hereinbefore defined, and R_4' represents an alkyl radical.

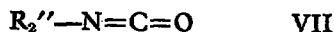
- When in general formula I R_1 represents a hydrogen atom or an alkyl radical, R_2 represents an alkyl, alkenyl, alkynyl, alkoxy or alkenyloxy radical and R_3 represents an alkyl radical, the oxadiazoline derivatives are prepared by reaction of a carbamoyl chloride of the general formula:—



VI

- 20 wherein R_2' represents an alkyl, alkenyl, alkynyl, alkoxy or alkenyloxy radical and R_3' represents an alkyl radical, with an amine of general formula II. The reaction is generally carried out in a basic organic solvent, for example pyridine, at a temperature between 10° and 60°C. It is also possible to carry out the reaction in an organic solvent, for example acetonitrile, methylene chloride or dimethylformamide, in the presence of a basic condensation agent such as pyridine.

- 30 When in general formula I R_1 represents a hydrogen atom or an alkyl radical, R_2 represents an alkyl, alkenyl or alkynyl radical and R_3 represents a hydrogen atom, the oxadiazoline derivatives are prepared by reaction of an isocyanate of the general formula:—

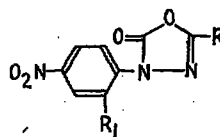


VII

- 40 wherein R_2'' represents an alkyl, alkenyl or alkynyl radical, with an amine of general formula II.

- The compounds of general formulae V and VI can be prepared in accordance with the usual methods for the preparation of carbamoyl chlorides from the corresponding amines.

- 45 The amines of general formula II wherein R_1 represents a hydrogen atom can be obtained by reduction of an oxadiazolone derivative of the general formula:—

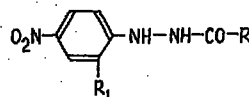


VIII

(wherein R and R_1 are as hereinbefore defined) 50 either by catalytic hydrogenation or by the action of iron in a dilute acid medium.

The amines of general formula II wherein R_1 represents an alkyl radical can be obtained by alkylation of an amine of general formula II, wherein R_1 represents a hydrogen atom, in accordance with known methods for the alkylation of primary amines. 55

The oxadiazolones of general formula VIII can be prepared by the reaction of phosgene with a hydrazide of the general formula:— 60



IX

wherein R and R_1 are as hereinbefore defined, in an inert organic solvent (e.g. an aromatic hydrocarbon, such as benzene or toluene, or an ether such as diethyl ether, or dioxan) or water at a temperature between 20° and 120°C. (see, for example, British Patent No. 1,063,799 granted to Rhone-Poulenc S.A. on an application filed Dec. 11, 1964). 65

The oxadiazoline derivatives of general formula I so obtained can optionally be purified by physical methods such as crystallisation or chromatography. 70

The new oxadiazoline derivatives of general formula I possess remarkable herbicidal properties. The herbicidal activity is shown against monocotyledons and dicotyledons on pre-emergence and post-emergence application. They are active against monocotyledons such as *Agrostis* spp., rye grass, couch grass and graminaceous plants in general; wheat and maize are resistant to them. Dicotyledons affected by them are, for example *Amaranthus* spp., *Chenopodium* spp., *Matricaria* spp., *Polygonum* spp., black nightshade and thistle. Furthermore, the oxadiazolines of general formula I possess a selective activity and can, for example, be used to destroy foxtail in wheat. The presently preferred class of oxadiazolines are those of general formula I wherein R represents an alkyl or phenyl radical, R_1 represents a hydrogen or halogen atom or a trifluoromethyl radical, R_2 represents an alkyl, alkynyl, alkoxy or alkenyloxy radical, R_3 represents an alkyl radical and R_4 represents a 85 90 95

hydrogen atom or an alkyl radical, and more particularly those compounds wherein R represents an alkyl radical of 2 to 4 carbon atoms (preferably t-butyl), R₁ represents a halogen atom or a trifluoromethyl radical, R₂ and R₃ are as just defined above, and R₄ represents a hydrogen atom. Of outstanding importance are 3 - [2 - chloro - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one, 3 - [2 - chloro - 4 - (3 - methyl - 3 - methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one, 3 - [2 - bromo - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one, 3 - [2 - trifluoromethyl - 4 - (3 - methyl - 3 - methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one, 3 - [2 - trifluoromethyl - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one, 3 - [2 - bromo - 4 - (3 - methyl - 3 - methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one and 3 - [2 - bromo - 4 - (3 - methyl - 3 - (1 - methyl - prop - 2 - ynyl) - ureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

According to a further feature of the present invention, there are provided herbicidal compositions containing, as the active ingredient, at least one oxadiazoline of general formula I in association with one or more diluent compatible with the oxadiazoline(s) and suitable for use in agricultural herbicidal compositions. These compositions can optionally contain other compatible pesticides, such as herbicides, insecticides or fungicides. Preferably the compositions contain between 0.05% and 80% by weight of oxadiazoline compound.

The compositions may be solid if there is employed a powdered solid compatible diluent such as talc, calcined magnesite, kieselguhr, tricalcium phosphate, powdered cork, adsorbent charcoal, or a clay such as kaolin or bentonite. These solid compositions are preferably prepared by grinding the oxadiazoline compound with the solid diluent, or by impregnating the solid diluent with a solution of the oxadiazoline compound in a volatile solvent, evaporating the solvent, and if necessary grinding the product so as to obtain a powder.

Instead of a solid diluent, there may be used a liquid in which the oxadiazoline compound is dissolved or dispersed. The compositions may thus take the form of suspensions, emulsions or solutions in organic or aqueous-organic media, for example aromatic hydrocarbons such as toluene or xylene, or mineral, animal or vegetable oils, or mixtures of these diluents. The compositions in the form of suspensions, emulsions or solutions may contain wetting, dispersing or emulsifying agents of the ionic or non-ionic type, for example sulphuricinate, quaternary ammonium derivatives or products based on condensates of ethylene oxide, such as the condensates of ethylene oxide with octylphenol, or fatty acid esters of anhydro-

sorbitols which have been rendered soluble by etherification of the free hydroxyl groups by condensation with ethylene oxide. It is preferable to use agents of the non-ionic type because they are not sensitive to electrolytes. When emulsions are required, the oxadiazolines may be used in the form of self-emulsifying concentrates containing the active substance dissolved in the emulsifying agent or in a solvent containing an emulsifying agent compatible with the oxadiazoline and solvent, a simple addition of water to such concentrates producing compositions ready for use.

The oxadiazoline derivatives of general formula I may be applied in doses of between 0.5 and 3 kg. per hectare according to the desired effect and the weed species to be treated.

The following Examples illustrate the preparation of the oxadiazoline derivatives of the present invention.

EXAMPLE 1

A solution of dimethylamine (2.25 g.) in anhydrous benzene (14 cc.) is added, at 20°C. and over the course of 10 minutes, to a suspension of 3 - (2 - chloro - 4 - isocyanatophenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (14.65 g.) in anhydrous benzene (36 cc.). As the reaction is exothermic, the temperature rises to 35°C. The medium becomes homogeneous and then a precipitate appears. Stirring is continued for 3 hours at 20°C., and the precipitate formed is filtered off and then dried under reduced pressure (0.5 mm.Hg) at 20°C. After recrystallisation from ethanol (175 cc.), 3 - [2 - chloro - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (13.45 g.), melting at 193°C., is obtained. 3 - (2 - Chloro - 4 - isocyanatophenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one can be prepared as follows:

3 - (2 - Chloro - 4 - amino - phenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (61.5 g.) is added to a 20% (w/v) solution (407 cc.) of phosgene in toluene. The mixture is then progressively heated under reflux until the evolution of gas ceases. The solvent is evaporated under reduced pressure (25 mm.Hg) at 60°C., and the residue is then dried to constant weight at 20°C. under reduced pressure (0.5 mm.Hg). 3 - (2 - Chloro - 4 - isocyanato - phenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (67.5 g.), melting at 63°C., is thus obtained.

The 3 - (2 - chloro - 4 - amino - phenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one starting material melting at 163°C., can be obtained by reduction (with iron in a dilute acid medium or by catalytic reduction) of 3 - (2 - chloro - 4 - nitro - phenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one melting at 102°C.

On following the same procedure, using suitable starting materials, the following products of general formula I are obtained:

Example No.	—R	R ₁ —	R ₂ —	R ₃ —	R ₄ —	Melting Point °C.
2	—C(CH ₃) ₃	H—	CH ₃ —	CH ₃ —	H—	188
3	—C(CH ₃) ₃	Cl—	CH ₃ —	C ₂ H ₅ —	H—	132
4	—C(CH ₃) ₃	Cl—	C ₂ H ₅ —	C ₂ H ₅ —	H—	138
5	—C(CH ₃) ₃	Cl—	CH ₃ O—	CH ₃ —	H—	128
6	—C(CH ₃) ₃	Br—	CH ₃ —	CH ₃ —	H—	202
7	—C(CH ₃) ₃	CF ₃ —	CH ₃ —	CH ₃ —	H—	191
8	—C(CH ₃) ₃	CF ₃ —	CH ₃ O—	CH ₃ —	H—	166
9	—(CH ₂) ₃ CH ₃	Cl—	CH ₃ —	CH ₃ —	H—	142
10	—C ₆ H ₅	Cl—	CH ₃ —	CH ₃ —	H—	203
11	—C ₂ H ₅	Cl—	CH ₃ —	CH ₃ —	H—	187
12	—C(CH ₃) ₃	Cl—	HC≡C—CH(CH ₃)—	CH ₃ —	H—	141
13	—C ₃ H ₇	Cl—	CH ₃ —	CH ₃ —	H—	179
14	—C(CH ₃) ₃	Br—	HC≡C—CH(CH ₃)—	CH ₃ —	H—	133
15	—C(CH ₃) ₃	I—	CH ₃ —	CH ₃ —	H—	214
16	—C(CH ₃) ₃	I—	CH ₃ O—	CH ₃ —	H—	156 then 170
17	—C(CH ₃) ₃	Br—	CH ₃ O—	CH ₃ —	H—	160
18	—C(CH ₃) ₃	I—	HC≡C—CH(CH ₃)—	CH ₃ —	H—	145
19	—CH ₂ CH(CH ₃) ₂	Cl—	C ₂ H ₅ —	C ₂ H ₅ —	H—	103
20	—CH ₂ CH(CH ₃) ₂	Cl—	CH ₃ —	CH ₃ —	H—	180
21	—CH ₂ CH(CH ₃) ₂	Cl—	CH ₃ O—	CH ₃ —	H—	106
22	—CH(CH ₃) ₂	Cl—	CH ₃ —	CH ₃ —	H—	168
23	—CH ₃	Cl—	CH ₃ —	CH ₃ —	H—	195
24	—CH ₃	Cl—	CH ₃ O—	CH ₃ —	H—	130

Example No.	-R	R ₁ -	R ₂ -	R ₃ -	R ₄ -	Melting Point °C.
25	-(CH ₂) ₃ CH ₃	CF ₃ -	CH ₃ -	CH ₃ -	H-	116
26	-CH(CH ₃) ₂	Cl-	CH ₃ O-	CH ₃ -	H-	100
27	-CH(CH ₃) ₂	Cl-	C ₂ H ₅ -	C ₂ H ₅ -	H-	110-112
28	-(CH ₂) ₃ CH ₃	CF ₃ -	CH ₃ O-	CH ₃ -	H-	82
29	-(CH ₂) ₃ CH ₃	CF ₃	C ₂ H ₅ -	C ₂ H ₅ -	H-	70-75
30	-C ₂ H ₅	Cl-	CH ₃ O-	CH ₃ -	H-	80
31	-C ₂ H ₅	Cl-	C ₂ H ₅ -	C ₂ H ₅ -	H-	100
32	-(CH ₂) ₂ CH ₃	Cl-	C ₂ H ₅ -	C ₂ H ₅ -	H-	93
33	-CH(CH ₃) ₂	CF ₃ -	CH ₃ O-	CH ₃ -	H-	102
34	-CH(CH ₃) ₂	CF ₃ -	CH ₃ -	C ₂ H ₅ -	H-	124
35	-CH ₂ CH(CH ₃) ₂	CF ₃ -	CH ₃ -	CH ₃ -	H-	117
36	-CH ₂ CH(CH ₃) ₂	CF ₃ -	CH ₃ O-	CH ₃ -	H-	82
37	-(CH ₂) ₂ CH ₃	Cl-	CH ₃ O-	CH ₃ -	H-	119
38	-C(CH ₃) ₃	Cl-	CH ₃ (CH ₂) ₃ -	CH ₃ -	H-	146-148
39	-CH(CH ₃) ₂	CF ₃ -	CH ₃ (CH ₂) ₃ -	CH ₃ -	H-	120
40	-CH(CH ₃) ₂	CF ₃ -	CH ₃ -	CH ₃ -	H-	155
41	-CH ₃	CF ₃ -	CH ₃ -	CH ₃ -	H-	156
42	-CH ₃	CF ₃ -	CH ₃ O-	CH ₃ -	H-	143
43	-CH ₃	CF ₃ -	CH ₃ (CH ₂) ₃ -	CH ₃ -	H-	102
44	-CH ₃	CF ₃ -	C ₂ H ₅ -	CH ₃ -	H-	124
45	-(CH ₂) ₃ CH ₃	Cl-	CH ₃ O-	CH ₃ -	H-	78
46	-(CH ₂) ₃ CH ₃	Cl-	C ₂ H ₅ -	CH ₃ -	H-	80-82
47	-(CH ₂) ₂ CH ₃	CF ₃ -	CH ₃ O-	CH ₃ -	H-	85
48	-C(CH ₃) ₃	CF ₃ -	C ₂ H ₅ -	CH ₃ -	H-	127
49	-C(CH ₃) ₃	Br-	C ₂ H ₅ -	C ₂ H ₅ -	H-	134
50	-(CH ₂) ₂ CH ₃	CF ₃ -	CH ₃ -	CH ₃ -	H-	96

Example No.	—R	R ₁ —	R ₂ —	R ₃ —	R ₄ —	Melting Point °C.
51	—(CH ₂) ₂ CH ₃	CF ₃ —	C ₂ H ₅ —	CH ₃ —	H—	97
52	—CH ₂ CH(CH ₃) ₂	Br—	CH ₃ —	CH ₃ —	H—	182
53	—CH ₂ CH(CH ₃) ₂	Br—	CH ₃ O—	CH ₃ —	H—	104
54	—(CH ₂) ₃ CH ₃	Br—	CH ₃ —	CH ₃ —	H—	143
55	—(CH ₂) ₃ CH ₃	Br—	CH ₃ O—	CH ₃ —	H—	89
56	—C(CH ₃) ₃	Br—	C ₂ H ₅ —	CH ₃ —	H—	131
57	—C(CH ₃) ₃	Cl—	CH ₃ —	H—	H—	169

EXAMPLE 58

Dimethylcarbamoyl chloride (5.65 g.) is added to a solution of 3 - (2 - chloro - 4 - amino - phenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (13.35 g.) in anhydrous pyridine (50 cc.). The reaction mixture is then heated at 40°C. for 8 hours. After cooling, the mixture is poured into water (250 cc.) and the precipitate which appears is filtered off, washed with water (3×50 cc.) and then taken up in methylene chloride (170 cc.). After decantation of the aqueous layer, hydrochloric acid (d=1.18; 4 cc.) is added to the organic layer, and then, after stirring for about 1 hour, the precipitate of the hydrochloride of the aminophenylloxadiazolone starting material which has formed is filtered off. The methylene chloride filtrate is washed with water (2×150 cc.) and then dried over anhydrous sodium sulphate. On evaporating the solvent at 50°C. under reduced pressure (25 mm.Hg), 3 - [2 - chloro - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (12.5 g.), melting at 191°C., is obtained.

EXAMPLE 59

A solution of O-allyl-N-methylhydroxylamine (8.7 g.) in water (200 cc.) is added over the course of about 10 minutes, with stirring, to a solution of 3 - (2 - chloro - 4 - isocyanatophenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (29.4 g.) in benzene (200 cc.) maintained at 20°C. After 30 minutes stirring, the precipitate which has formed is filtered off, washed with benzene (3×100 cc.) and then dried at 50°C. under reduced pressure (0.5 mm.Hg). 3 - [2 - Chloro - 4 - (3 - methyl - 3 - allyloxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (32 g.), melting at 142°C., is obtained. After recrystallisation from ethanol, the product melts at 143°C.

EXAMPLE 60

A solution of 3 - (2 - chloro - 4 - methylaminophenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (10.2 g.) in anhydrous benzene (27 cc.) is added over the course of about 10 minutes to a mixture cooled to about 2°C. of anhydrous benzene (45 cc.), a 28% (w/v) solution (12.7 cc.) of phosgene in toluene, and triethylamine (3.6 g.). The reaction mixture is stirred for 1 hour at 3°C and then there is added, at 3°C. and over the course of 30 minutes, a 10.2% (w/v) solution (35 cc.) of dimethylamine in benzene. Stirring is continued for 3 hours at a temperature between 3° and 5°C., and then water (70 cc.) is added to the reaction mixture. The organic phase is decanted, washed with water (5×70 cc.) and dried over sodium sulphate. On concentration at 55°C. under reduced pressure (15 mm.Hg), there is obtained a viscous oil which is purified by chromatography through a column of silica. 3 - [2 - Chloro - 4 - (1,3,3 - trimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one (8.3 g.) is thus isolated in the form of a light yellow viscous mass.

3 - (2 - Chloro - 4 - methylaminophenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one, melting at 110°C., can be prepared by acetylation, sodation, methylation and then hydrolysis of 3 - (2 - chloro - 4 - aminophenyl) - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

The following Example illustrates herbicidal compositions according to the present invention.

EXAMPLE 61

A wettable powder containing 50% by weight of active product is prepared in the following manner:

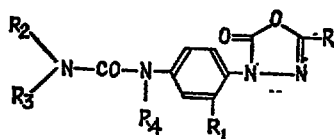
1 part of Tween 80 (mono-oleate of a polyoxyethylene derivative of sorbitol), 20 parts of calcium lignosulphite and 29 parts of kiesel-

- guhr 23 are added to 50 parts of 3 - [2-chloro - 4 - (3,3 - dimethylureido)phenyl] - 5-t - butyl - 1,3,4 - oxadiazol - 2 - one, the parts being by weight. "Tween" is a registered Trade Mark.

- Following grinding and sieving, the powder obtained is used, after dilution with water, to destroy weeds such as those hereinbefore mentioned specifically.
- According to another feature of the invention, a method of controlling the growth of weeds at a locus comprises applying to the locus a herbicidally-effective quantity of an oxadiazoline derivative of general formula I.
- The oxadiazoline may be applied to a crop-growing area, the amount of applied oxadiazoline then being sufficient for control of the weed, e.g. foxtail, but insufficient to cause substantial damage to the crop, e.g. wheat or maize. The dosage can vary in accordance with the weed or weeds to be controlled, the crop and the desired effect. In general, dosages of active material of 0.5 to 3 kg. per hectare give good results.

WHAT WE CLAIM IS:—

1. Oxadiazoline derivatives of the general formula:—



- wherein R represents an alkyl or phenyl radical, or a phenyl radical carrying at least one substituent selected from halogen atoms, and alkyl and alkoxy radicals; R₁ represents a hydrogen or halogen atom, or an alkyl, alkoxy, nitro or trifluoromethyl radical; R₂ represents a hydrogen atom or an alkyl, alkenyl, alkynyl, alkoxy or alkenyloxy radical; R₃ represents a hydrogen atom or an alkyl radical, and R₄ represents a hydrogen atom or an alkyl radical, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkenyl, alkynyl and alkenyloxy radicals containing 2 to 4 carbon atoms.

2. Oxadiazoline derivatives according to claim 1 wherein R represents an alkyl or phenyl radical, R₁ represents a hydrogen or halogen atom or a trifluoromethyl radical, R₂ represents an alkyl, alkenyl, alkoxy or alkenyloxy radical, R₃ represents an alkyl radical and R₄ represents a hydrogen atom or an alkyl radical, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkynyl and alkenyloxy radicals containing 2 to 4 carbon atoms.

3. Oxadiazoline derivatives according to claim 1 wherein R represents an alkyl radical of 2 to 4 carbon atoms, R₁ represents a halogen

atom or a trifluoromethyl radical, R₂ represents an alkyl, alkenyl, alkoxy or alkenyloxy radical, R₃ represents an alkyl radical and R₄ represents a hydrogen atom, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkynyl and alkenyloxy radicals containing 2 to 4 carbon atoms.

4. Oxadiazoline derivatives according to claim 1 wherein R₂ represents a hydrogen atom, or an alkyl, alkenyl, alkynyl or alkoxy radical, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkenyl and alkynyl radicals containing 2 to 4 carbon atoms.

5. Oxadiazoline derivatives according to any one of the preceding claims wherein R represents the t-butyl radical.

6. 3 - [2 - Chloro - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

7. 3 - [2 - Chloro - 4 - (3 - methyl - 3-methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

8. 3 - [2 - Bromo - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

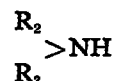
9. 3 - [2 - Trifluoromethyl - 4 - (3 - methyl - 3 - methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

10. 3 - [2 - Trifluoromethyl - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

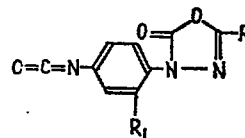
11. 3 - [2 - Bromo - 4 - (3 - methyl - 3-methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

12. 3 - [2 - Bromo - 4 - (3 - methyl - 3-(1 - methylprop - 2 - ynyl) - ureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

13. Process for the preparation of oxadiazoline derivatives of the general formula specified in claim 1 which comprises (A) when R, R₁, R₂ and R₃ are as defined in claim 1 and R₄ represents a hydrogen atom, reacting an amine of the general formula:—



(wherein R₂ and R₃ are as defined in claim 1) with an isocyanate of the general formula:—



(wherein R and R₁ are as defined in claim 1), or

(B) when R, R₁, R₂ and R₃ are as defined in claim 1 and R₄ represents an alkyl radical, reacting an amine of the general formula:—

guhr 23 are added to 50 parts of 3 - [2-chloro - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one, the parts being by weight. "Tween" is a registered Trade Mark.

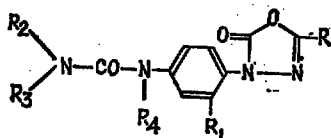
Following grinding and sieving, the powder obtained is used, after dilution with water, to destroy weeds such as those hereinbefore mentioned specifically.

According to another feature of the invention, a method of controlling the growth of weeds at a locus comprises applying to the locus a herbicidally-effective quantity of an oxadiazoline derivative of general formula I.

The oxadiazoline may be applied to a crop-growing area, the amount of applied oxadiazoline then being sufficient for control of the weed, e.g. foxtail, but insufficient to cause substantial damage to the crop, e.g. wheat or maize. The dosage can vary in accordance with the weed or weeds to be controlled, the crop and the desired effect. In general, dosages of active material of 0.5 to 3 kg. per hectare give good results.

WHAT WE CLAIM IS:—

1. Oxadiazoline derivatives of the general formula:—



wherein R represents an alkyl or phenyl radical, or a phenyl radical carrying at least one substituent selected from halogen atoms, and alkyl and alkoxy radicals; R₁ represents a hydrogen or halogen atom, or an alkyl, alkoxy, nitro or trifluoromethyl radical; R₂ represents a hydrogen atom or an alkyl, alkenyl, alkynyl, alkoxy or alkenyloxy radical; R₃ represents a hydrogen atom or an alkyl radical, and R₄ represents a hydrogen atom or an alkyl radical, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkenyl, alkynyl and alkenyloxy radicals containing 2 to 4 carbon atoms.

2. Oxadiazoline derivatives according to claim 1 wherein R represents an alkyl or phenyl radical, R₁ represents a hydrogen or halogen atom or a trifluoromethyl radical, R₂ represents an alkyl, alkenyl, alkoxy or alkenyloxy radical, R₃ represents an alkyl radical and R₄ represents a hydrogen atom or an alkyl radical, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkynyl and alkenyloxy radicals containing 2 to 4 carbon atoms.

3. Oxadiazoline derivatives according to claim 1 wherein R represents an alkyl radical of 2 to 4 carbon atoms, R₁ represents a halogen

atom or a trifluoromethyl radical, R₂ represents an alkyl, alkenyl, alkoxy or alkenyloxy radical, R₃ represents an alkyl radical and R₄ represents a hydrogen atom, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkynyl and alkenyloxy radicals containing 2 to 4 carbon atoms.

4. Oxadiazoline derivatives according to claim 1 wherein R₂ represents a hydrogen atom, or an alkyl, alkenyl, alkynyl or alkoxy radical, the alkyl and alkoxy radicals containing 1 to 4 carbon atoms, and the alkenyl and alkynyl radicals containing 2 to 4 carbon atoms.

5. Oxadiazoline derivatives according to any one of the preceding claims wherein R represents the t-butyl radical.

6. 3 - [2 - Chloro - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

7. 3 - [2 - Chloro - 4 - (3 - methyl - 3-methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

8. 3 - [2 - Bromo - 4 - (3,3 - dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

9. 3 - [2 - Trifluoromethyl - 4 - (3 - methyl - 3 - methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

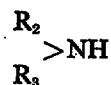
10. 3 - [2 - Trifluoromethyl - 4 - (3,3-dimethylureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

11. 3 - [2 - Bromo - 4 - (3 - methyl - 3-methoxyureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

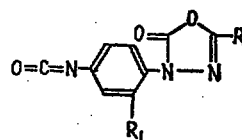
12. 3 - [2 - Bromo - 4 - (3 - methyl - 3-(1 - methylprop - 2 - ynyl) - ureido)phenyl] - 5 - t - butyl - 1,3,4 - oxadiazol - 2 - one.

13. Process for the preparation of oxadiazoline derivatives of the general formula specified in claim 1 which comprises

(A) when R, R₁, R₂ and R₃ are as defined in claim 1 and R₄ represents a hydrogen atom, reacting an amine of the general formula:—

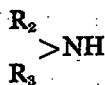


(wherein R₂ and R₃ are as defined in claim 1) with an isocyanate of the general formula:—

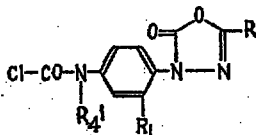


(wherein R and R₁ are as defined in claim 1), or
(B) when R, R₁, R₂ and R₃ are as defined in claim 1 and R₄ represents an alkyl radical, reacting an amine of the general formula:—

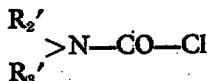




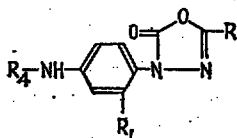
(wherein R_2 and R_3 are as defined in claim 1) with a compound of the general formula:—



- 5 (wherein R and R_1 are as defined in claim 1 and R_4' represents an alkyl radical), or
(C) when R , R_1 and R_4 are as defined in claim 1, R_2 represents an alkyl, alkenyl, alkynyl, alkoxy or alkenyloxy radical and R_3 represents an alkyl radical, reacting a carbamoyl chloride of the general formula:—



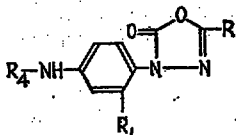
- 15 (wherein R_2' represents an alkyl, alkenyl, alkynyl, alkoxy or alkenyloxy radical and R_3' represents an alkyl radical) with an amine of the general formula:—



- (wherein R , R_1 and R_4 are as defined in claim 1), or
20 (D) when R , R_1 and R_4 are as defined in claim 1, R_2 represents an alkyl, alkenyl or alkynyl radical and R_3 represents a hydrogen atom, reacting an isocyanate of the general formula:—



(wherein R_2'' represents an alkyl, alkenyl or alkynyl radical) with an amine of the general formula:—



- 30 (wherein R , R_1 and R_4 are as defined in claim 1), the alkyl and alkoxy radicals containing 1 to 4 carbon atoms and the alkenyl, alkynyl and alkenyloxy radicals containing 2 to 4 carbon atoms.

- 35 14. Process for the preparation of oxadiazoline derivatives of the general formula specified in claim 1 substantially as hereinbefore described.

15. Process for the preparation of oxadiazoline derivatives of the general formula specified in claim 1 substantially as hereinbefore described in Examples 1 to 9. 40

16. Process for the preparation of oxadiazoline derivatives of the general formula specified in claim 1 substantially as described in any one of Examples 10 to 60. 45

17. Oxadiazoline derivatives of the general formula specified in claim 1 when prepared by the process claimed in claim 13, 14, 15 or 16.

18. Herbicidal compositions which comprise, as active ingredient, at least one oxadiazoline derivative as claimed in any one of claims 1 to 3 and 5 in association with one or more diluents compatible with the oxadiazoline and suitable for use in herbicidal compositions. 50 55

19. Herbicidal compositions which comprise, as active ingredient, at least one oxadiazoline derivative as claimed in claim 4 in association with one or more diluents compatible with the oxadiazoline and suitable for use in herbicidal compositions. 60

20. Herbicidal compositions according to claim 18 or 19 in which the quantity of oxadiazoline is between 0.05% and 80% by weight of the composition. 70

21. Herbicidal compositions according to claim 18, 19 or 20 which contain a wetting, dispersing or emulsifying agent.

22. Herbicidal compositions according to claim 21 in which the wetting, dispersing or emulsifying agent is a non-ionic compound. 75

23. Herbicidal compositions according to any one of claims 18 to 22 in which a diluent for the oxadiazoline derivative is water.

24. Herbicidal compositions according to any one of claims 19 to 23 wherein the oxadiazoline active ingredient in the composition is one or more of the compounds claimed in claims 6 to 10. 80

25. Herbicidal compositions according to any one of claims 18 and 20 to 23 wherein the oxadiazoline active ingredient in the composition is one or both of the compounds claimed in claims 11 and 12. 85

26. Herbicidal compositions comprising one or more oxadiazoline compounds of the general formula specified in claim 1 substantially as hereinbefore described with especial reference to Example 61. 90

27. A method of controlling the growth of monocotyledenous and dicotyledenous weeds at a locus which comprises applying to the locus a herbicidally-effective quantity of an oxadiazoline derivative in a herbicidal composition as claimed in any one of claims 18 to 26. 95 100

28. A method according to claim 27 in which the herbicidal composition is applied to a crop-growing area at a rate sufficient to control the growth of weeds without causing substantial permanent damage to the crop. 105

29. A method according to claim 28 in which



- the crop-growing area contains wheat or maize.
30. A method according to claim 27, 28 or
29 in which the herbicidal composition is
applied to the locus so as to give 0.5 to 3 kg.
5 of oxadiazoline derivative per hectare.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

