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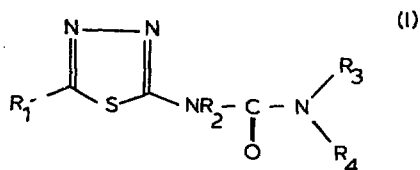


(54) NEW 1,3,4-THIADIAZOLYL UREAS

(71) We, AGRIPAT S.A. a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, 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:—

The present invention concerns new 1,3,4-thiadiazolyl ureas, processes for their production, also herbicidal compositions, which contain as active substances such ureas, and processes for controlling weeds and wild grasses using the new active substances or compositions which contain them.

The 1,3,4-thiadiazolyl ureas of the present invention correspond to the formula I:



wherein

- R_1 represents a perfluoroalkyl radical with 1 or 2 carbon atoms,
 R_2 represents hydrogen or an alkyl radical having 1 to 4 carbon atoms,
 R_3 represents hydrogen or an alkyl radical having 1 to 4 carbon atoms with the proviso that at least one of the symbols R_2 and R_3 represents hydrogen, and
 R_4 represents an alkyl radical having 1 to 4 carbon atoms which is unsubstituted or substituted by a substituent selected from chlorine, bromine, cyano, alkoxy having 1 to 3 carbon atoms and alkylthio having 1 to 3 carbon atoms; an

[Price 25p]

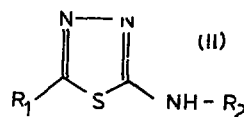
alkenyl or alkynyl radical with 3 or 4 carbon atoms, a cycloalkyl radical with 3 to 6 carbon atoms, or an alkoxy radical having 1 to 3 carbon atoms.

In formula I in the definition of R_1 , the perfluoroalkyl radical denotes preferably the trifluoromethyl radical. Preferably alkyl radicals R_2 , R_3 and R_4 are methyl or ethyl radicals.

In one embodiment the invention provides 1,3,4-thiadiazolyl ureas of the formula I above in which R_1 and R_2 have the above defined meanings, R_3 is hydrogen and R_4 is an alkyl radical having 1 to 4 carbon atoms which is unsubstituted or substituted by chlorine, bromine or by an alkoxy or alkylthio radical having 1 to 3 carbon atoms, or is a cycloalkyl radical having 3 to 6 carbon atoms.

In another embodiment the invention provides 1,3,4-thiadiazolyl ureas of the formula I above in which R_1 has the meanings defined above, R_2 is hydrogen and when R_3 is an alkyl radical having 1 to 4 carbon atoms, R_4 is an alkyl radical having 1 to 4 carbon atoms or an alkoxy radical having 1 to 3 carbon atoms and when R_3 is hydrogen R_4 is an alkenyl radical having 3 or 4 carbon atoms or a cyanoalkyl radical.

The new 1,3,4-thiadiazolyl ureas of formula I are produced according to the invention by reacting a 2-amino-1,3,4-thiadiazole of the formula II:



wherein

R_1 and R_2 have the meanings given under

Price 33p

be obtained from corresponding fluoroacyl thiosemicarbazides by ring-closure reaction with polyphosphoric acid in accordance with the process described by E. Hoggarth in J. Chem. Soc. 1949, 1163—1167. Fluoroacyl thiosemicarbazides have not been known hitherto. They are obtained by reacting equimolar amounts of a corresponding aliphatic fluorocarboxylic acid derivative, particularly the anhydride, with a thiosemicarbazide optionally in the presence of a solvent or diluent. 4-Alkylthiosemicarbazides are known compounds. To obtain 1,3,4-thiadiazoles, the fluoroacyl thiosemicarbazides can be used as such or produced *in situ*.

As fluoroacylthiosemicarbazides the following, for example, can be used:

- 1-trifluoroacetylthiosemicarbazide,
- 1 - trifluoroacetyl - 4 - methylthiosemicarbazide,
- 1 - trifluoroacetyl - 4 - ethylthiosemicarbazide,
- 1 - trifluoroacetyl - 4 - isopropyl - thiosemicarbazide,
- 1 - trifluoroacetyl - 4 - n - butyl - thiosemicarbazide,
- 1 - pentafluoropropionylthiosemicarbazide.

The new 1,3,4-thiadiazolyl ureas of the formula I possess excellent herbicidal properties and can be used in concentrations of from 0.1 to 35 kg per hectare for controlling mono- and dicotyl weeds and wild forms of grass. In high concentrations, the new ureas act as total herbicides, and in lower concentrations, i.e. of from 0.1 to 5 kg per hectare, they act as selective herbicides. Deep rooted types of weeds and those difficult to control, e.g. leguminosae and umbelliferous plants are attacked by these active substances. They can be applied equally successfully both as pre-emergence and post-emergence agents. It is thus possible to destroy or prevent field weeds such as, e.g. *Panicum* sp., *Sinapis* sp., *Chenopodiaceae*, *Alopecurus* sp., *Matricaria* sp., without causing damage to cultivated plants, such as corn.

The new 1,3,4-thiadiazolyl ureas of the formula I are used, mixed with usual additives, as herbicidal compositions. Moreover, the new active substances can also be mixed with fertilizers and applied in this form. In order to broaden the range of activity of the ureas according to the invention, they can be applied in admixture with other herbicides: e.g. with halogen-, alkoxy- and alkylthio-diamino-s-triazines; halogenated phenols, nitrophenols, aliphatic, aromatic and araliphatic carboxylic acids as well as with the salts of such compounds; ureas, carbamic acid esters, uracils, inorganic salts, such as

- 2 - chloro - 4,6 - bis - (ethylamino) - s-triazine,

- 2 - chloro - 4 - ethylamino - 6 - isopropylamino - s - triazine,
- 2 - chloro - 4,6 - bis - (methoxypropylamino) - s - triazine,
- 2 - methoxy - 4,6 - bis - (isopropylamino)-s-triazine,
- 2 - diethylamino - 4 - isopropylacetamido-6 - methoxy - s - triazine,
- 2 - isopropylamino - 4 - methoxypropylamino - 6 - methylmercapto - s - triazine,
- 2 - methylmercapto - 4,6 - bis - (isopropylamino) - s - triazine,
- 2 - methylmercapto - 4,6 - bis - (ethylamino) - s - triazine,
- 2 - methylmercapto - 4 - ethylamino - 6 - isopropylamino - s - triazine,
- 2 - methoxy - 4,6 - bis - (ethylamino) - s-triazine,
- 2 - methoxy - 4 - ethylamino - 6 - isopropylamino - s - triazine,
- 2 - chloro - 4,6 - bis - (isopropylamino)-s - triazine,
- dinitro - sec. - butyl phenol and salts thereof,
- pentachlorophenol and salts thereof,
- 2,3,6 - trichlorobenzoic acid and salts thereof,
- 2,3,5,6 - tetrachlorobenzoic acid and salts thereof,
- 2 - methoxy - 3,5,6 - trichlorobenzoic acid and salts thereof,
- 2 - methoxy - 3,6 - dichlorobenzoic acid and salts thereof,
- 3 - amino - 2,5 - dichlorobenzoic acid and salts thereof,
- 3 - nitro - 2,5 - dichlorobenzoic acid and salts thereof,
- 2 - methyl - 3,6 - dichlorobenzoic acid and salts thereof,
- 2,4 - dichlorophenoxyacetic acid and salts and esters thereof,
- 2,4,5 - trichlorophenoxyacetic acid and salts and esters thereof,
- (2 - methyl - 4 - chlorophenoxy) - acetic acid and salts and esters thereof,
- 2 - (2,4,5 - trichlorophenoxy) - propionic acid and salts and esters thereof,
- 2 - (2,4,5 - trichlorophenoxy) ethyl - 2,2-dichloropropionic acid esters,
- 4 - (2,4 - dichlorophenoxy) - butyric acid and salts and esters thereof,
- 4 - (2 - methyl - 4 - chlorophenoxy) - butyric acid and salts and esters thereof,
- 2,3,6 - trichlorobenzoyloxypropanol,
- 2,6 - dichlorobenzonitrile,
- trichloroacetic acid and salts thereof,
- 2,2 - dichloropropionic acid and salts thereof,
- 2,3,6 - trichlorophenyl - acetic acid and salts thereof,
- 2 - chloro - N,N - diallyl - acetamide,
- 3 - (3,4 - dichlorophenyl) - 1,1 - dimethyl-urea,

- 3 - (4 - chlorophenyl) - 1,1 - dimethyl-urea,
 3 - phenyl - 1,1 - dimethyl - urea,
 3 - (3,4 - dichlorophenyl) - 3 - methoxy-
 1,1 - dimethyl urea,
 5 3 - (3,4 - dichlorophenyl) - 1 - n - butyl-
 1 - methyl - urea,
 3 - (3,4 - dichlorophenyl) - 1 - methoxy-
 1 - methyl - urea,
 10 3 - (4 - chlorophenyl) - 1 - methoxy - 1-
 methyl - urea,
 3 - (3,4 - dichlorophenyl) - 1,1,3 - tri-
 methyl - urea,
 3 - (3,4 - dichlorophenyl) - 1,1 - diethyl-
 urea,
 15 3 - (4 - chlorophenoxyphenyl) - 1,1 - di-
 methyl - urea,
 ethyl N,N - di - (n - propyl)-thiocarb-
 amate,
 20 n - propyl N,N - di - (n - propyl) - thio-
 carbamate,
 ethyl N - ethyl - N - (n - butyl) - thio-
 carbamate,
 n - propyl N - ethyl - N - (n - butyl)-
 thiocarbamate,
 25 isopropyl N - phenyl - carbamate,
 isopropyl N - (m - chlorophenyl) - carb-
 amate,
 4 - chloro - 2 - butynyl N - (m - chloro-
 phenyl) - carbamate,
 30 maleic hydrazide.

The following examples describe the pro-
 duction of new 1,3,4-thiadiazolyl ureas of the
 formula I. The temperatures are given in
 35 degrees centigrade.

EXAMPLE 1.

- a) A mixture of 91.1 g of thiosemicarba-
 zide and 125 g of trifluoroacetic acid in a
 sulphonating flask is heated to reflux tempera-
 40 ture (72°). 1 kg of polyphosphoric acid is
 then added cautiously with stirring.

- The reaction mixture is kept at the reflux
 temperature of trifluoroacetic acid until all of
 the latter is bound. The reaction mixture is
 45 then slowly heated to 130°, and, after keeping
 it for 1 hour at this temperature, cooled to
 80°. The mixture is poured into about 3 l of
 ice water and the reaction product precipitated
 by adding concentrated sodium hydroxide
 50 solution (until pH 5—6). The crude product
 is recrystallised from aqueous ethanol. The 2-
 amino - 5 - trifluoromethyl - 1,3,4 - thia-
 diazole thus obtained melts at 212—214°.

- b) To the solution of 6.75 g of 2-amino-
 55 5 - trifluoromethyl - 1,3,4 - thiadiazole in 10
 ml of dimethyl formamide at about 50—60°,
 2.8 ml of methyl isocyanate are added. Fol-
 lowing completion of the reaction, the N-[5-
 trifluoromethyl - 1,3,4 - thiadiazolyl(2)] - N'-
 60 methyl urea separates in crystalline form.
 Melting point 186—189°.

EXAMPLE 2.

- a) 46.8 g of trifluoroacetic acid anhydride

are added dropwise at 0° to a suspension of
 27.3 g of 4-methyl-thiosemicarbazide in 300
 ml of ether. The mixture is then stirred for
 8 hours at room temperature. After cooling,
 the reaction product is separated and washed
 with a little cold ether. The 1 - trifluoroacetyl-
 4 - methyl - thiosemicarbazide thus obtained
 70 melts at 163—164°.

b) 25 g of 1 - trifluoroacetyl - 4 - methyl-
 thiosemicarbazide are introduced in portions
 within 15 minutes into 125 g of polyphos-
 phoric acid at 80°. The reaction mixture is
 then heated to 120° and stirred for about 30
 minutes at this temperature. The reaction mix-
 ture, previously cooled to about 70°, is then
 poured into 500 ml of ice-water, and the pro-
 duct is precipitated by adding aqueous concen-
 trated ammonia solution, separated and
 washed with water. After recrystallising from
 ethanol/water, the 2 - methylamino - 5 - tri-
 fluoromethyl - 1,3,4 - thiadiazole has a melt-
 ing point of 115—116°.

c) 12 g of 2 - methylamino - 5 - trifluoro-
 methyl - 1,3,5 - thiadiazole are dissolved at
 about 50—60° in 30 ml of dimethyl form-
 amide, and 4 g of methyl isocyanate are then
 added. Following completion of the reaction,
 the N - [5 - trifluoromethyl - 1,3,4 - thia-
 diazyl(2)] - N,N' - dimethyl urea separates
 in crystalline form. Melting point 134°.

EXAMPLE 3.

a) 31.5 g of phenyl chloroformate are added
 dropwise at room temperature to a suspension
 of 34 g of 2 - amino - 5 - trifluoromethyl-
 1,3,4 - thiadiazole in 300 ml of acetonitrile
 and 20 g of triethylamine. The mixture is
 stirred for 15 hours at room temperature and
 subsequently evaporated to dryness in vacuo.
 The residue is taken up in 100 ml of water
 and heated for 15 minutes on a steam bath.
 After cooling, the crystalline precipitate is
 separated and recrystallised in methanol. The
 phenyl N - [5 - trifluoromethyl - 1,3,4 - thia-
 diazyl(2)] - carbamate has a melting point
 of 180 to 182°.

b) Gaseous dimethylamine is passed at 80°
 through the suspension of 14.5 g of phenyl
 N - [5 - trifluoromethyl - 1,3,4 - thiadiazyl-
 (2)] - carbamate in 300 ml of benzene until
 the reaction is completed. The course of the
 reaction is observed by means of thin layer
 chromatography. The N - [5 - trifluoro-
 methyl - 1,3,4 - thiadiazyl - (2)] - N',N'-
 dimethyl urea crystallises from the reaction
 mixture. Melting point 159—160°.

The same compound is obtained when the
 corresponding S-phenyl thiocarbamate is pre-
 pared according to Example 3, a) and then
 reacted as described above under b).

In the manner described in the previous
 examples, the following 1,3,4 - thiadiazolyl
 ureas are obtained.

TABLE I

No.	Compound	Melting point
1	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-ethyl urea	180—181°
2	N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)] - N' - isopropyl urea	158—161°
3	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-n-butyl urea	152—154°
4	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-cyclohexyl urea	175—177°
5	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-cyclopropyl urea	191—192°
6	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N',N'-diethyl urea	110—113°
7	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(3)]-N'-methoxy-N'-methyl urea	108°
8	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-methyl-N'-1'-methylpropargyl urea	129°
9	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-(α -cyano- α -methyl-ethyl)urea	171°
10	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'- β -methoxyethyl urea	169°
11	N-([5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'- β -methyl-thioethyl urea	132°
12	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-allyl urea	160°
13	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-sec.-butyl urea	118°
14	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-methyl-N'- β -chloroethyl urea	113°
15	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-methyl-N'- β -methoxyethyl urea	70°
16	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-methyl-N'-n-butyl urea	67°
17	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-methyl-N'-cyclohexyl urea	111°
18	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-methyl-N'-cyclopropyl urea	111°
19	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-ethyl-N'-methyl urea	128°
20	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-ethyl-N'-isopropyl urea	99°
21	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-ethyl-N'-n-butyl urea	61°
22	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N,N'-diethyl urea	78°
23	N-[5-pentafluoroethyl-1,3,4-thiadiazolyl(2)]-N'-methyl urea	157°

TABLE I (Continued)

No.	Compound	Melting point
24	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-isopropyl-N-isopropyl - N' - methyl urea	
25	N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-n-butyl-N'-methyl urea	

5 The production of herbicidal compositions according to the invention is carried out in a known manner by the intimate mixing and grinding of the active substances of formula I with suitable carriers, optionally with the addition of dispersion agents or solvents which are inert to the active substances. The active substances can be used for the production of

10 dusts, sprinkling agents, granulates, coated granules, impregnated granules, homogeneous granules, wettable powders, pastes, emulsions, aerosols and solutions. In general from 0.5 to 80% by weight of such compositions may consist of the active substance depending on the carrier or diluent.

To produce the solid forms for application (dusts, sprinkling agents, granulates), the active substances are mixed with solid carriers.

20 Examples of carriers are kaolin, talcum, bole, loess, chalk, limestone, ground limestone, ataclay, dolomite, diatomaceous earth, precipitated silicic acid, alkaline earth silicates, sodium and potassium aluminium silicates

25 (feldspar and mica), calcium and magnesium sulphates, magnesium oxide, ground synthetic plastics; fertilisers, such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea; ground vegetable products,

30 such as cereal-flour, bark-flour, sawdust, ground nut shells, cellulose powder, residues from plant extractions; active charcoal, used either alone or as mixtures.

The grain-size of the carriers is, for dusts advantageously up to about 0.1 mm, for sprinkling agents about 0.075 to 0.2 mm and for granulates from 0.2 mm upwards.

The concentrations of active substances in the solid preparations may be 0.5 to 80% by weight.

40 To these mixtures additives can also be added which stabilise the active substance and/or non-ionic, anion-active and cation-active substances, which for example improve the adhesiveness of the active substances on plants and parts of plants (adhesives) and/or ensure better wettability (wetting agents) and also dispersibility (dispersing agents). The following are examples of adhesives:

50 olein-chalk mixture, cellulose derivatives (methyl cellulose, carboxymethyl cellulose), hydroxy-ethylglycol ethers of mono- and dialkyl-phenols having 5—15 ethylene oxide radicals per molecule and 8—9 carbon atoms in the alkyl radical, lignin-sulphonic acids, the alkali and alkaline earth metal salts thereof, polyethylene-

glycol ethers, fatty alcohol polyethyleneglycol ethers having 5—20 ethylene oxide radicals per molecule and 8—18 carbon atoms in the fatty alcohol part, condensation products of ethylene oxide, propylene oxide, polyvinylpyrrolidones, polyvinyl alcohols, condensation products of urea-formaldehyde as well as latex products.

Active substance concentrates dispersible in carrier, optional additives which stabilise the water, i.e. wettable powders, pastes and emulsion concentrates, are compositions which can be diluted with water to give any desired concentration. They consist of active substance, active substance, surface-active substances and anti-foaming agents and, optionally, solvents. The concentration of active substance in these compositions may be 5—80% by weight.

Wettable powders and pastes are obtained by mixing and grinding the active substances with dispersing agents and pulverulent carriers in suitable devices until a homogeneous mixture is obtained. Carriers which can be employed are for example those mentioned above for solid preparations. In some cases it is advantageous to use mixtures of different carriers. The following can be used for example as dispersing agents: condensation products of sulphonated naphthalene and sulphonated naphthalene derivatives with formaldehyde, condensation products of naphthalene or naphthalene sulphonic acids with phenol and formaldehyde, also alkali, ammonium and alkaline earth metal salts of lignin sulphonic acid, and also alkylaryl sulphonates, alkali and alkaline earth metal salts of dibutyl naphthalene sulphonic acid, fatty alcohol sulphates, salts of sulphated fatty alcohol glycol ether, sodium oleoylethionate, sodium oleoylmethyl-tauride, ditertiary acetylene glycols, dialkyl dilauryl ammonium chloride and fatty acid alkali and alkaline earth metal salts. Suitable as anti-foaming agents are for example silicones.

The active substances are mixed, ground, sieved and strained with the above mentioned additives in such a way that the grain-size of the solid material does not exceed 0.02—0.04 mm in the case of the wettable powders and 0.03 mm in the case of pastes. To produce the emulsion concentrates and pastes, dispersing agents, such as those described in the previous sections, organic solvents and water are used. Suitable solvents are, e.g. alcohols, benzene, xylenes, toluenes, dimethyl sulphoxide

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and mineral oil fractions having a boiling point between 120 and 350°. The solvents should preferably be practically without smell, not phytotoxic, inert to the active substances and not readily inflammable.

5 In addition, the compositions according to the invention can be applied in the form of solutions. In this case, the active substance, or several active substances, of formula I are dissolved in suitable organic solvents, mixtures of solvents or water. Suitable for use as organic solvents are aliphatic and aromatic hydrocarbons, chlorinated derivatives thereof, alkyl naphthalene or mineral oils. The solutions contain the active substances in a concentration of between 1% and 20% by weight.

Other biocidally active substances or agents can be mixed with the above-described compositions according to the invention. Thus the new compositions may contain, in addition to the aforesaid compounds of formula I, e.g. insecticides, other fungicides, bactericides, fungistatics, bacteriostatics or nematocides to give a wider effective range.

25 The compositions according to the invention can also contain plant fertilizers and trace elements.

The following examples serve to illustrate the forms of application of the new ureas. The terms "part" and % denote parts and % by weight.

Granulate

30 The following materials are used to produce a 5% granulate:

- 5 parts of N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N',N'-diethyl urea,
- 0.25 part of epichlorohydrin,
- 0.25 part of cetyl polyethylene glycol ether with 8 moles of ethylene oxide,
- 40 3.50 parts of polyethylene glycol (molecular weight 380—420),
- 91 parts of kaolin (grain size 0.3—0.8 mm).

45 The active substance is mixed with heptachlorohydrin and dissolved in 6 parts of acetone. Polyethylene glycol and cetyl polyethyleneglycol ether are then added. The solution thus obtained is sprayed on to kaolin and then evaporated in vacuo.

Wettable powder

The following constituents are used to produce a) a 50%, b) a 25% and c) a 10% wettable powder, respectively:

- 55 a) 50 parts of N[5-trifluoromethyl-1,3,4-thiadiazolyl(2)] - N - ethyl - N'-methyl urea,
- 5 parts of sodium dibutyl naphthalene sulphonate,
- 60 3 parts of naphthalene sulphonate/phenol sulphonate acid/formaldehyde condensate (3:2:1),
- 20 parts of kaolin,
- 22 parts of Champagne chalk;

- b) 25 parts of N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-methyl urea, 65
- 5 parts of sodium oleylmethyltauride,
- 2.5 parts of naphthalene sulphonate/formaldehyde condensate,
- 0.5 part of carboxymethyl cellulose, 70
- 5 parts of neutral potassium aluminium silicate,
- 62 parts of kaolin;
- c) 10 parts of N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N,N'-dimethyl urea, 75
- 3 parts of mixture of the sodium salts of saturated fatty alcohol sulphates (with 12 to 18 carbon atoms),
- 5 parts of naphthalene sulphonate/formaldehyde condensate, 80
- 82 parts of kaolin.

The active substance is added to the appropriate carriers (kaolin and chalk) and then mixed and ground with the additives. Wettable powders are obtained exhibiting excellent wettability and suspension properties. Suspensions of any desired concentration of active substance can be obtained from such a wettable powder by dilution with water. Such suspensions are used for controlling weeds and wild grasses in cultivated plantations.

Paste

The following materials are used to produce a 45% paste:

- 45 parts of N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]N',N'-dimethyl urea, 95
- 5 parts of sodium aluminum silicate,
- 14 parts of cetyl polyethylene glycol ether with 8 moles of ethylene oxide,
- 1 part of cetyl polyethylene glycol ether with 5 moles of ethylene oxide, 100
- 2 parts of spindle oil,
- 10 parts of polyethylene glycol (molecular weight 380—420),
- 23 parts of water. 105

The active substance is intimately mixed and ground, in suitable equipment, with the additives. A paste is obtained from which suspensions of any desired concentration can be prepared by dilution with water. The suspensions are suitable for the treatment of vegetable plantations.

Emulsion concentrate

The following constituents are mixed together to produce a 10% emulsion concentrate:

- 10 parts of N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]N'-ethyl urea,
- 15 parts of oleyl polyethylene glycol ether with 8 moles of ethylene oxide, 120
- 75 parts of isophorone.

This concentrate can be diluted with water to give emulsions of required concentration. Such emulsions are suitable for controlling weeds in cultivated plantations, such as e.g. cotton and maize.

The following 1,3,4-thiadiazolyl ureas are

used as test compounds to determine their herbicidal activity:

1. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N'-methyl urea
- 5 2. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N',N'-dimethyl urea
3. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N',N'-diethyl urea
- 10 4. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N'-isopropyl urea
5. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N'-allyl urea
6. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N-methyl-N'-cyclopropyl urea
- 15 7. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N'-cyclohexyl urea
8. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N' - methyl - N' - 1 - methyl-propargyl urea
- 20 9. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N'-2-methoxyethyl urea
10. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)] - N - methyl - N' - 2 - chloroethyl urea
- 25 11. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N-methyl-N'-n-butyl urea
12. N - [5 - trifluoromethyl - 1,3,4 - thiadiazolyl(2)]-N,N'-dimethyl urea

a) Germination test

Method:

The active substance is mixed with an inert carrier (talcum) in a ratio of 1:9 and the resultant 10%-formulation is mixed with garden soil. The active substance is applied in a concentration of 0.5 g per liter of soil. The soil is filled into flower pots, and oats, ray grass, mustard and vetch are sowed therein. The results observed 20 days after sowing are expressed according to the following values:

10 = normal growth

9—1 = graduated increase in damage

0 = all plants destroyed.

b) Contact test

Method:

Flowerpots filled with soil are sowed with oats and mustard. The active substance is applied in the form of an emulsion prepared from a 25% emulsion concentrate. The concentration is 0.5 g of active substance in 100 ml of water per m². The treatment is effected when the mustard reaches the 4—6 leaf stage. The results are observed 14 days after treatment and are expressed as above under a).

Results of germination and contact tests

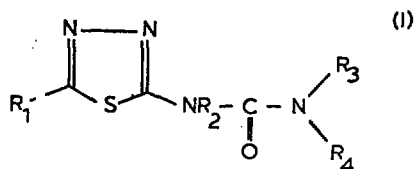
active substance	Germination test (effect after 20 days)				Contact test (effect after 14 days)	
	oats	ray grass	mustard	vetch	oats	mustard
1	0	0	0	0	2	1
2	0	0	0	0	0	0
3	0	0	0	1	8	2
4	0	0	0	4	9	0
5	0	0	0	0	9	2
6	0	0	0	0	6	1
7	—	—	—	—	1 (Galium)*	0 (camomile)*
8	1	0	0	0	—	—
9	0	0	0	0	—	—
10	1	1	0	0	—	—
11	0	0	0	0	6	1
12	0	0	0	0	0 (Galium)*	0

*Used instead of oats or mustard.



WHAT WE CLAIM IS:—

1. 1,3,4-thiadiazolyl ureas of the formula I:



wherein

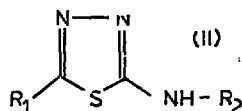
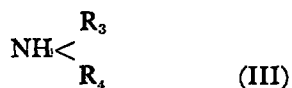
5 R_1 represents a perfluoroalkyl radical with 1 or 2 carbon atoms, R_2 represents hydrogen or an alkyl radical having 1 to 4 carbon atoms,10 R_3 represents hydrogen or an alkyl radical having 1 to 4 carbon atoms with the proviso that at least one of the symbols R_1 and R_3 represents hydrogen, and15 R_4 represents an alkyl radical having 1 to 4 carbon atoms which is unsubstituted or is substituted by a substituent selected from chlorine, bromine, cyano, alkoxy having 1 to 3 carbon atoms, alkyl thio having 1 to 3 carbon atoms; an alkenyl or alkynyl radical with 3 or 4 carbon atoms, a cycloalkyl radical with 3 to 6 carbon atoms, or an alkoxy radical having 1 to 3 carbon atoms.

2. The compound N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N'-methyl urea.

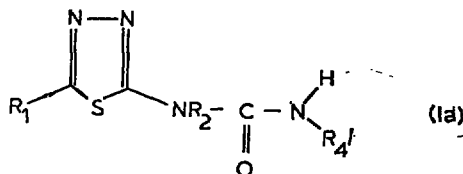
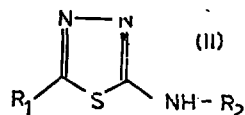
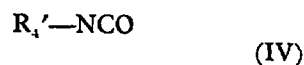
3. The compound N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N,N'-dimethyl urea.

4. The compound N-[5-trifluoromethyl-1,3,4-thiadiazolyl(2)]-N-ethyl-N'-methyl urea.

30 5. The compound N-[5-trifluoromethyl-1,3,4 - thiadiazolyl(2)] - N' - methyl - N'-methoxy urea.

6. Process for the production of 1,3,4-thiadiazolyl ureas of the formula I set forth in claim 1 wherein R_1 , R_2 , R_3 and R_4 have the meanings defined in claim 1 which comprises reacting in the presence of a solvent or diluent a 2-amino-1,3,4-thiadiazole of the formula II40 wherein R_1 and R_2 have the meanings defined in claim 1 with a haloformic acid ester or a halothioformic acid S-ester in the presence of an acid-binding agent to form the carbamic acid derivative and reacting the latter with an amine of the formula III:wherein R_3 and R_4 have the meanings given under formula I.

7. Process for the production of 1,3,4-thiadiazolyl ureas of the formula Ia:

wherein R_1 and R_2 have the meanings defined in claim 1 and R_4' represents an alkyl radical having 1 to 4 carbon atoms which is unsubstituted or substituted by a substituent selected from chlorine, bromine and alkoxy and alkylthio radicals having 1 to 3 carbon atoms; or a cycloalkyl radical with 3 to 6 carbon atoms, characterised by reacting in the presence of a solvent or diluent a 2-amino-1,3,4-thiadiazole of the formula IIwherein R_1 and R_2 have the meanings defined in claim 1 with an isocyanate of the formula IV:wherein R_4' has the meanings defined above under formula Ia.

8. A process as claimed in claim 6 in which the halothioformic acid ester is a phenyl chloroformate.

9. A process as claimed in claim 6 in which the halothioformic acid S-ester is a phenyl chlorothioformate.

10. A herbicidal composition, which comprises from 0.5 to 80% by weight of a herbicidal active substance which consists of one or more 1,3,4-thiadiazolyl ureas of formula I in claim 1, and dispersing agents and/or carriers for the said substance.

11. Process for controlling weeds and wild grasses, characterised by the application of 1,3,4-thiadiazolyl ureas of formula I in claim 1, or of compositions according to claim 10.

12. 1,3,4-Thiadiazolyl ureas, of the formula set forth in claim 1 in which R_1 and R_2 have the meanings defined in claim 1 and R_3 is hydrogen and R_4 is an alkyl radical having 1 to 4 carbon atoms which is unsubstituted or substituted only by chlorine, bromine or by an alkoxy or alkylthio radical having 1 to 3 carbon atoms or a cycloalkyl radical having 3 to 6 carbon atoms.13. 1,3,4-Thiadiazolyl ureas of the formula set forth in claim 1 in which R_1 has the meanings defined in claim 1, R_2 is hydrogen and when R_3 is an alkyl radical having 1 to 4 carbon atoms, R_4 is an alkyl radical having

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- 1 to 4 carbon atoms or an alkoxy radical having 1 to 3 carbon atoms and when R_3 is hydrogen R_4 is an alkenyl radical having 3 or 4 carbon atoms or a cyano-alkyl radical.
- 5 14. Compounds as claimed in claim 12 substantially as hereinbefore described in Example 1 or 2.
15. Compounds as claimed in claim 13
- substantially as hereinbefore described in Example 3.

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