

PATENT SPECIFICATION

(11) 1 230 432

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NO DRAWINGS

- (21) Application No. 41320/68 (22) Filed 29 Aug. 1968
 (31) Convention Application No. F 53531 IVd/12p
 (32) Filed 19 Sept. 1967 in
 (33) Germany (DT)
 (45) Complete Specification published 5 May 1971
 (51) International Classification C 07 d 91/62; A 01 n 9/14
 (52) Index at acceptance
 C2C 172—192—282 200 215 220 22Y 247 256 25Y
 30Y 313 31Y 339 340 341 342 34Y 373 37Y
 577 578 579 601 603 614 626 627 62X 72X
 72Y 791 79Y KA KD KF RB RE
 A5E 1C4B2 1C4B3 1C4B4
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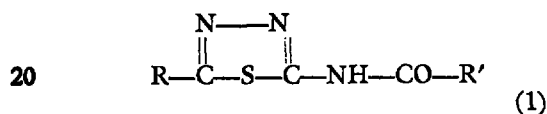
(54) N-SUBSTITUTED 5-AMINO-1,3,4-THIADIAZOLES

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of the Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to certain new N-substituted 5 - amino - 1,3,4 - thiadiazoles, to a process for their production and to their use as herbicides.

It is already known that thiazolyl ureas, e.g. N - (4 - methyl - 1,3 - thiazolyl - 2) - N' - methyl urea, can be used as herbicides (Belgian Patent Specification 679 138).

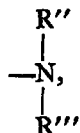
The invention provides new N-substituted 5 - amino - 1,3,4 - thiadiazoles of the formula:—



in which

R is hydrogen, alkyl, alkenyl, cycloalkyl or alkylmercapto,

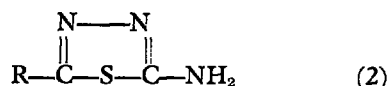
R' is alkyl, alkenyl, chloroalkyl, alkoxy, aryloxy or



R'' is hydrogen, alkyl or alkoxy, and R''' is alkyl or alkenyl.

The invention also provides a process for the production of the compounds of Formula [Price 25p]

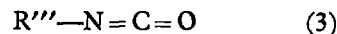
(1) in which a 5 - amino - 1,3,4 - thiadiazole of the formula:—



in which

R has the meaning stated above,

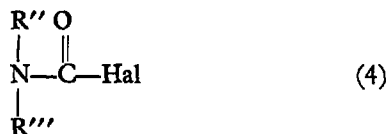
(a) is reacted, optionally, in the presence of a solvent, with an isocyanate of the formula:—



in which

R''' has the meaning stated above, or

(b) is reacted, in the presence of an acid binder, with an acid halide of the formula:—



in which

R'' and R''' have the meaning stated above, and

Hal is halogen (preferably chlorine), or

(c) is reacted, in the presence of an acid binder, with an acid halide of the formula:—

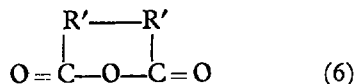


in which

R' has the meaning stated above with the proviso that it is not —NR''R''', and

Hal is halogen (preferably chlorine), or

(d) is reacted with an acid anhydride of the formula:—



in which

5 R' has the meaning stated above with the proviso that it is not —NR''R'''.

The process, especially process variant (a), may be carried out in an inert solvent; the term solvent including mere diluents.

10 It is decidedly surprising that the new 1,3,4-thiadiazoles exhibit a stronger herbicidal activity, and, in particular, also better selective herbicidal effects, than the previously known thiadiazoles.

15 The new 1,3,4-thiadiazoles are clearly characterised by the formula (1) stated above.

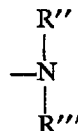
In the above formulae, R is preferably hydrogen, alkyl with 1—4 carbon atoms, alkenyl with 3 carbon atoms, cycloalkyl with

20 5 or 6 carbon atoms or alkylmercapto with

1—4 carbon atoms.

R' is preferably alkyl with 1—4 carbon atoms, alkenyl with 2—4 carbon atoms, chloroalkyl with 1—4 carbon atoms and 1—3 chlorine atoms, alkoxy with 1—4 carbon atoms, phenoxy or

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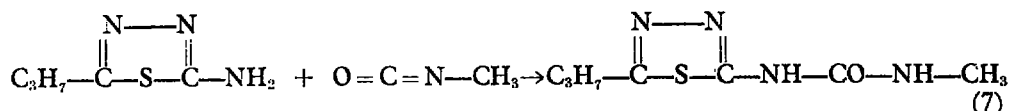
R'' is preferably hydrogen, alkyl with 1—4 carbon atoms or alkoxy with 1—2 carbon atoms, and

R''' is preferably alkyl with 1—4 carbon atoms or alkenyl with 2—4 carbon atoms.

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If 3-propyl-5-amino-1,3,4-thiadiazole and methyl isocyanate are used as starting materials, the reaction according to (a) can be represented by the following formula scheme:

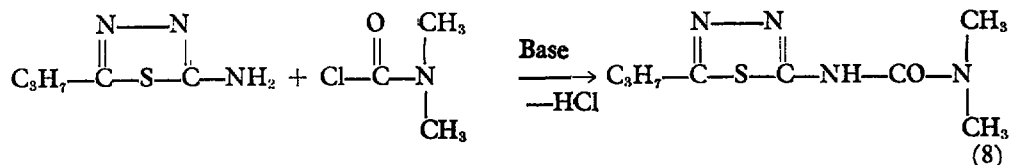
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If dimethylcarbamic acid chloride is reacted with the same thiadiazole, the reaction according

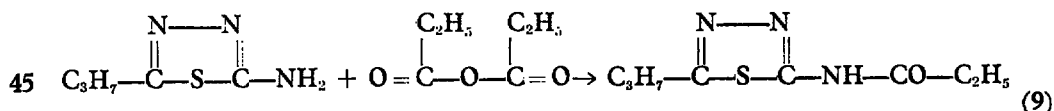
ing to (b) can be represented by the following formula scheme:—

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Process (c) proceeds in analogous manner.

The reaction according to (d) corresponds to the following formula scheme:



Some the aminothiadiazoles of Formula (2) are already known. New thiadiazoles can be prepared in the same manner as those already known, for example by reaction of the appropriate 1-acylthiosemicarbazides with agents which split off water, such as acetic anhydride (Chemischer Bericht 29, 2511 (1896)).

50 The starting materials (3), (4), (5) and (6) are also known.

55 Examples of the preferred isocyanates which can be used are methyl isocyanate, ethyl isocyanate and isopropyl isocyanate.

Examples of the preferred acid chlorides which can be used are dimethylcarbamyl chloride, propionyl chloride, monochloroacetyl chloride, dichloroacetyl chloride and methyl chloroformate.

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As solvents, all inert organic solvents are suitable. Preferred solvents include hydrocarbons, such as benzene, toluene; ethers, such as diethyl ether, dioxan, tetrahydrofuran; chlorinated hydrocarbons, such as methylene chloride, chloroform, carbon tetrachloride; ketones, such as acetone; esters, such as ethyl

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acetate and acetonitrile, and dimethyl formamide.

As acid binders, all customary acid-binding agents can be used. Preferred agents include the alkali metal hydroxides, alkali metal carbonates and tertiary amines. Particularly suitable are sodium hydroxide, sodium carbonate, triethyl amine and pyridine.

The reaction temperatures can be varied within a fairly wide range. In general, the work is carried out from 0° to 140°C, preferably from 10° to 120°C.

When carrying out the process, approximately equimolar amounts of starting materials are generally used. The working up of the reaction mixture is carried out in the usual manner.

The active compounds according to the invention influence plant growth and can therefore be used for defoliation or for desiccation of the green parts of plants. In this case they serve as harvest auxiliaries to facilitate harvesting. They are, however, quite particularly suitable for the control of weeds. By weeds in the widest sense are meant all plants which grow in places where they are not desired. Whether the substances according to the invention act as total or selective herbicides depends essentially on the amount applied.

The substances according to the invention can be used for example in the case of the following plants: dicotyledons, such as mustard (*Sinapis*), cress (*Lepidium*), cleaver (*Galium*), common chickweed (*Stellaria*), mayweed (*Matricaria*), small-flower Galinsoga (*Galinsoga*), fathen (*Chenopodium*), stinging nettles (*Urtica*), groundsel (*Senecio*), cotton (*Gossypium*), beets (*Beta*), beans (*Phaseolus*), carrots (*Daucus*), potatoes (*Solanum*), coffee (*Coffea*); monocotyledons, such as timothy (*Phleum*), bluegrass (*Poa*), fescue (*Festuca*), goosegrass (*Eleusine*), foxtail (*Setaria*), ryegrass (*Lolium*), cheat (*Bromus*), barnyard grass (*Echinochloa*), maize (*Zea*), rice (*Oryza*), oats (*Avena*), barley (*Hordeum*), wheat (*Triticum*), millet (*Panicum*), and sugar cane (*Saccharum*).

The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents. In the case of the use of water as an extender, organic solvents, can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes or benzene, chlorinated aromatic hydrocarbons, such as chlorobenzenes, paraffins, such as mineral oil fractions, alcohols, such as methanol or butanol, or strongly polar solvents, such as dimethyl formamide or di-

methyl sulphoxide, as well as water.

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc or chalk, or ground synthetic minerals, such as highly-dispersed silicic acid or silicates.

Preferred examples of emulsifying agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates and aryl sulphonates; and preferred examples of dispersing agents include lignin, sulphite waste liquors and methyl cellulose.

The active compounds according to the invention may be present in the formulations in admixture with other active compounds.

The formulations contain, in general, from 0.1 to 95, preferably 0.5 to 90, per cent by weight of active compound.

The active compounds may be used as such, in the form of their formulations or of the application forms prepared therefrom, such as ready-to-use solutions, emulsions, suspensions, powders, pastes and granulates. Application takes place in the usual manner, for example by watering, spraying, atomising, dusting or scattering.

The active compounds according to the invention can be used according to both the pre-emergence method and the post-emergence method, that is, before or after emergence of the plants.

When the active compounds are used according to the pre-emergence method, the amount applied can be varied within fairly wide ranges. In general, it lies from 1 to 50 kg per hectare. When used according to the post-emergence process, the concentration of active compound can also be varied within fairly wide ranges. In general, it lies from 0.01 to 5%, preferably from 0.25 to 1% by weight.

Thus the invention also provides a herbicidal composition containing as active ingredient a thiadiazole of the formula (1) in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The invention also provides a method of combating weeds which comprise applying to the weeds or to a weed habitat a thiadiazole of the formula (1) alone or in the form of a composition containing as active ingredient a thiadiazole of the formula (1) in admixture with a solid or liquid diluent or carrier.

The present invention further provides a method of providing a harvested crop which comprises applying a compound of the present invention to the area of cultivation of the crop whereby the latter is protected from damage by weeds, and harvesting the crop.

The invention also provides a method of defoliating plants which comprises applying to the plants a thiadiazole of the formula (1) alone or in admixture with a solid or liquid

diluent or carrier whereby the leaves of the plants are caused to fall off or die.

- 5 The effectiveness of the new thiadiazoles according to the formula (1) is demonstrated by the tests in Examples A and B.

The process of the invention is demonstrated in the following Examples 1—4.

EXAMPLE A

Pre-emergence test

- 10 Solvent. 5 parts by weight acetone
Emulsifier: 1 part by weight alkylaryl polyglycol ether.

- 15 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is then diluted with water to the desired concentration.

- 20 Seeds of the test plants are sown in normal soil and, after 24 hours, watered with the preparation of the active compound. It is excellent

to keep constant the amount of water per unit area. The concentration of the active compound in the preparation is of no importance, only the amount of active compound applied per unit area being decisive. After three weeks, the degree of damage to the test plants is determined and characterised by the values 0—5, which have the following meaning:

- 0 no effect
1 slight damage or delay in growth
2 marked damage or inhibition of growth
3 heavy damage and only deficient development or only 50% emerged
4 plants partially destroyed after germination or only 25% emerged
5 plants completely dead or not emerged.

The active compounds, the amounts applied and the results obtained can be seen from the following Table 1:—

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TABLE 1
pre-emergence test

Active compound	Amount of active compound applied kg/hectare	Echinochloa	Chenopodium	Sinapis	Cotton	Wheat
$\begin{array}{c} \text{CH}_3-\text{C}-\text{N} \\ \parallel \\ \text{HC}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NHCH}_3 \\ \text{(known)} \end{array}$	40 20 10 5 2.5	4-5 4 4 3 2	5 5 5 4 2-3	5 5 4 2-3 1	4 4 3 1 0	4-5 4 4 3 1
$\begin{array}{c} \text{CH}_3 \quad \text{N}-\text{N} \\ \quad \parallel \\ \text{CH}_3-\text{CH}-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \\ \parallel \\ \text{N} \end{array}$	40 20 10	5 5 5	5 5 5	5 5 5	5 3 3	5 5 5
$\begin{array}{c} \text{N}-\text{N} \\ \parallel \\ \text{CH}_3-\text{S}-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \\ \parallel \\ \text{N} \end{array}$	5 2.5	5 4	5 4-5	5 5	1 0	4 3
$\begin{array}{c} \text{CH}_3-\text{S}-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \\ \parallel \\ \text{N} \end{array}$	40 20 10 5 2.5	5 5 5 5 5	5 5 5 5 5	5 5 5 5 5	5 5 5 3 3	4-5 4-5 4-5 3 0

plants is determined and characterised by the values 0-5, which have the following meaning:

- 0 no effect
1 a few slightly burnt spots
2 marked damage to leaves
3 some leaves and parts of stalks partially dead
4 plant partially destroyed
5 plant completely dead

The active compounds, their concentrations and the results obtained can be seen from the following Table 2:—

EXAMPLE B

Post-emergence test

Solvent: 5 parts by weight acetone

5 Emulsifier: 1 part by weight alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is then diluted with water to the desired concentration.

10 Test plants which have a height of about 5-15 cm. are sprayed with the preparation of the active compound until just dew moist.

15 After three weeks, the degree of damage to the

TABLE 2
post-emergence test

Active compound	Concentration of active compound % by weight	Echino- chloa	Cheno- podium	Sinapis	Stellaria	Galini- soga	Daucus	Oats	Cotton	Wheat
$\begin{array}{c} \text{CH}_3-\text{C}-\text{N} \\ \parallel \\ \text{HC}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \end{array}$ (10)	0.2 0.1 0.05 0.025	5 4 3 1	5 5 4-5 3	5 5 4-5 4	5 4-5 3 2	5 5 4-5 3	5 3 1 0	2 1-2 1 0	3 2-3 2 0	2 1-2 1 0
$\begin{array}{c} \text{N}-\text{N} \\ \parallel \\ \text{n-C}_3\text{H}_7-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \end{array}$ (13)	0.2 0.1 0.05 0.025	5 5 3 1	5 5 4-5 3	5 5 5 5	5 5 4 4	5 5 4-5 3	5 5 4 3	5 5 4-5 3	4 4 3 2	3 3 3 2
$\begin{array}{c} \text{CH}_3 \text{ N}-\text{N} \\ \parallel \parallel \\ \text{CH}_3-\text{CH}-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \end{array}$ (11)	0.2 0.1 0.05 0.025	4-5 4-5 4-5 4-5	5 5 5 5	5 5 5 5	5 5 5 4-5	5 5 5 5	5 5 5 4	5 5 5 0	4-5 4 2 1	5 3 2 0
$\begin{array}{c} \text{N}-\text{N} \\ \parallel \parallel \\ \text{CH}_3-\text{S}-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \end{array}$ (12)	0.2 0.1 0.05 0.025	5 5 5 4-5	5 5 5 5	5 5 5 5	5 5 5 5	5 5 5 5	5 5 5 5	4-5 4 4 4	5 5 4-5 4-5	2 1 0 0
$\begin{array}{c} \text{N}-\text{N} \\ \parallel \parallel \\ \text{n-C}_4\text{H}_9-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3 \end{array}$ (14)	0.2 0.1 0.05 0.025	5 5 5 4-5	5 5 5 5	5 5 5 5	5 5 5 5	5 5 5 5	5 5 5 5	5 5 5 5	5 5 4-5 4-5	2 1-2 0 0
$\begin{array}{c} \text{N}-\text{N} \\ \parallel \parallel \\ \text{CH}_3\text{S}-\text{C}-\text{S}-\text{C}-\text{NH}-\text{CO}-\text{C}_2\text{H}_5 \end{array}$ (15)	0.2 0.1 0.05 0.025	5 5 4 3	5 5 5 4	5 5 5 5	5 5 5 5	5 5 5 5	5 5 5 5	4-5 3 3 1	5 5 3 1	3 1 0 0

EXAMPLE 1

5 To 14.9 g (0.1 mole) 2 - propyl - 5 - amino - 1,3,4 - thiadiazole dissolved in 100 ml dimethyl formamide there are added dropwise, at 20°C, 5.7 g (0.1 mole) methyl isocyanate. After the subsidence of the heat effect, stirring is continued for 1 hour at 50°C, distillation to one half of the original volume is then

effected in a vacuum, followed by pouring into 400 ml of water. The crude N - (3 - propyl - 1,3,4 - thiadiazolyl) - N' - methyl urea is obtained in solid form and is filtered off with suction. 10

In an analogous manner, the further ureas mentioned in Table 3 were also prepared. 15

TABLE 3

R	R''	R'''	m.p. °C.
(16) CH ₃	H	CH ₃	259
(17) CH ₃	H	C ₂ H ₅	156
(18) C ₂ H ₅	H	CH ₃	178
(19) n-C ₃ H ₇	H	C ₂ H ₅	98
(11) isoC ₃ H ₇	H	CH ₃	147
(20) isoC ₃ H ₇	H	C ₂ H ₅	172
(21) CH ₃ -CH=CH	H	CH ₃	196
(12) CH ₃ S	H	CH ₃	212
(22) CH ₃ S	H	C ₂ H ₅	136
(23) CH ₃ S	H	n-C ₃ H ₇	125
(24) CH ₃ S	H	CH ₂ -CH=CH ₂	196
(14) n-C ₄ H ₉ S	H	CH ₃	154

EXAMPLE 2

20 To 28.6 g (0.2 mole) 2 - isopropyl - 5 - amino - 1,3,4 - thiadiazole in 200 ml dioxan there are added 20.2 g (0.2 mole) triethyl amine, and 22.6 g (0.2 mole) chloroacetyl chloride are slowly added dropwise at 20°C. Stirring is then effected for 2 hours at 50°C,

followed by suction filtration from the precipitate, and the filtrate is stirred into 400 ml of water. The N - (2 - isopropyl - 1,3,4 - thiadiazolyl) - chloroacetamide separates in solid form. 25

In analogous manner, the further amides mentioned in Table 4 were also prepared. 30

TABLE 4

R	R'	m.p. °C.
(25) isoC ₃ H ₇	CH ₂ Cl	196
(26) CH ₃	CH ₂ Cl	185
(27) CH ₃	CHCl ₂	241
(28) C ₂ H ₅	CHCl ₂	183
(29) n-C ₃ H ₇	CH ₂ Cl	225
(30) CH ₃ S	CH ₂ Cl	221
(31) n-C ₄ H ₉	CH ₂ Cl	163

EXAMPLE 3

To 28.6 g (0.2 mole) 2 - propyl - 5 - amino - 1,3,4 - thiadiazole in 200 ml dioxan there are added 20.2 g (0.2 mole) triethyl amine, and 18.9 g (0.2 mole) methyl chloroformate are added dropwise at 40°C. Stirring is then effected for 2 hours at 60°C. Thereafter, suction filtration from the triethylamine

hydrochloride is effected and the filtrate is evaporated. N - (2 - propyl - 1,3,4 - thiadiazolyl) - methylcarbamate is obtained in solid form.

In analogous manner, the further carbamates and ureas mentioned in Table 5 were also prepared.

TABLE 5

R	R'	R''	R'''	m.p. °C.
(32) CH ₃	CH ₃ O			234
(33) C ₂ H ₅	CH ₃ O			177
(34) n-C ₃ H ₇	CH ₃ O			138
(35) n-C ₃ H ₇	C ₆ H ₅ O			187
(36) iso-C ₃ H ₇	CH ₃ O			114
(37) iso-C ₃ H ₇	C ₆ H ₅ O			196
(38) n-C ₃ H ₇		CH ₃	CH ₃	71
(39) iso-C ₃ H ₇		CH ₃	CH ₃	65
(40) n-C ₃ H ₇	iso-C ₃ H ₇ O			78

EXAMPLE 4

To 28.6 (0.2 mole) 2 - propyl - 5 - amino - 1,3,4 - thiadiazole are added 26 g (0.2 mole) propionic anhydride, and heated at 120°C for 3 hours. After evaporation of the propionic

acid, the N - (2 - propyl - 1,3,4 - thiadiazolyl) - propionamide remains in solid form.

In analogous manner, the further amides mentioned in Table 6 were also prepared.

TABLE 6

R	R'	m.p. °C.
(41) n-C ₃ H ₇	C ₂ H ₅	192
(42) CH ₃	C ₂ H ₅	265
(43) C ₂ H ₅	C ₂ H ₅	225
(44) iso-C ₃ H ₇	C ₂ H ₅	194
(15) CH ₃ S	C ₂ H ₅	174
(45) n-C ₄ H ₉ S	C ₂ H ₅	145

WHAT WE CLAIM IS:—

1. N-substituted 5 - amino - 1,3,4 - thiadiazoles of the formula:—

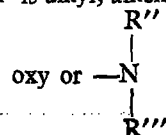


(1)

in which

R is hydrogen, alkyl, alkenyl, cycloalkyl or alkylmercapto,

R' is alkyl, alkenyl, chloroalkyl, alkoxy, aryl-





EXAMPLE 3

5 To 28.6 g (0.2 mole) 2 - propyl - 5 - amino - 1,3,4 - thiadiazole in 200 ml dioxan there are added 20.2 g (0.2 mole) triethyl amine, and 18.9 g (0.2 mole) methyl chloroformate are added dropwise at 40°C. Stirring is then effected for 2 hours at 60°C. Thereafter, suction filtration from the triethylamine

hydrochloride is effected and the filtrate is evaporated. N - (2 - propyl - 1,3,4 - thia- 10 diazoly) - methylcarbamate is obtained in solid form.

In analogous manner, the further carbamates and ureas mentioned in Table 5 were also pre- 15 pared.

TABLE 5

R	R'	R''	R'''	m.p. °C.
(32) CH ₃	CH ₃ O			234
(33) C ₂ H ₅	CH ₃ O			177
(34) n-C ₃ H ₇	CH ₃ O			138
(35) n-C ₃ H ₇	C ₆ H ₅ O			187
(36) isoC ₃ H ₇	CH ₃ O			114
(37) isoC ₃ H ₇	C ₆ H ₅ O			196
(38) n-C ₃ H ₇		CH ₃	CH ₃	71
(39) isoC ₃ H ₇		CH ₃	CH ₃	65
(40) n-C ₃ H ₇	isoC ₃ H ₇ O			78

EXAMPLE 4

20 To 28.6 (0.2 mole) 2 - propyl - 5 - amino - 1,3,4 - thiadiazole are added 26 g (0.2 mole) propionic anhydride, and heated at 120°C for 3 hours. After evaporation of the propionic

acid, the N - (2 - propyl - 1,3,4 - thia- azoly) - propionamide remains in solid form.

In analogous manner, the further amides mentioned in Table 6 were also prepared. 25

TABLE 6

R	R'	m.p. °C.
(41) n-C ₃ H ₇	C ₂ H ₅	192
(42) CH ₃	C ₂ H ₅	265
(43) C ₂ H ₅	C ₂ H ₅	225
(44) iso-C ₃ H ₇	C ₂ H ₅	194
(15) CH ₃ S	C ₂ H ₅	174
(45) n-C ₄ H ₉ S	C ₂ H ₅	145

WHAT WE CLAIM IS:—

1. N-substituted 5 - amino - 1,3,4 - thia- azoles of the formula:—

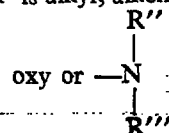


(1)

in which

R is hydrogen, alkyl, alkenyl, cycloalkyl or alkylmercapto,

R' is alkyl, alkenyl, chloroalkyl, alkoxy, aryl-



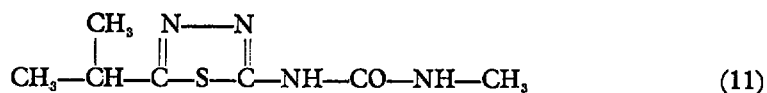
R'' is hydrogen, alkyl or alkoxy, and
R''' is alkyl or alkenyl.

2. Thiadiazoles according to claim 1 in
which R is hydrogen, alkyl with 1—4 carbon
atoms, alkenyl with 3 carbon atoms, cycloalkyl
with 5—6 carbon atoms or alkylmercapto with
1—4 carbon atoms; R' is alkyl with 1—4
carbon atoms, alkenyl with 2—4 carbon atoms,
chloroalkyl with 1—4 carbon atoms and 1—3
chlorine atoms, alkoxy with 1—4 carbon

atoms, phenoxy or $\begin{array}{c} R'' \\ | \\ -N- \\ | \\ R''' \end{array}$; R'' is hydrogen,
alkyl with 1—4 carbon atoms or alkoxy with
1—2 carbon atoms, and R''' is alkyl with 1—4
carbon atoms or alkenyl with 2—4 carbon
atoms.

3. The thiadiazole of the formula:—

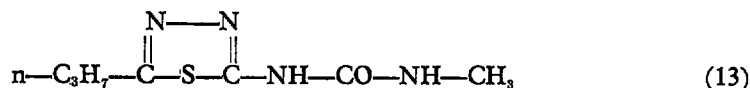
15



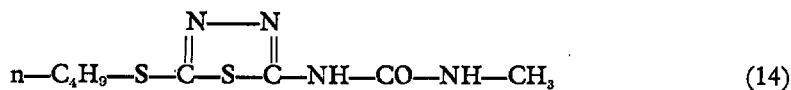
4. The thiadiazole of the formula:—



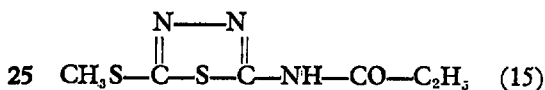
5. The thiadiazole of the formula:—



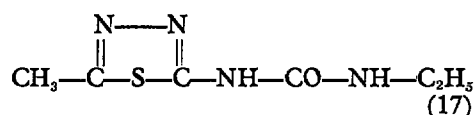
6. The thiadiazole of the formula:—



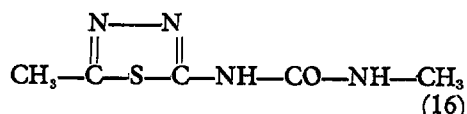
7. The thiadiazole of the formula:—



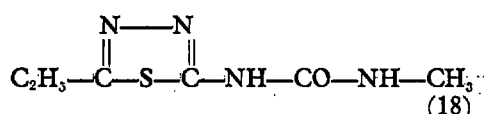
9. The thiadiazole of the formula:—



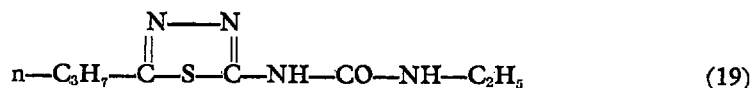
8. The thiadiazole of the formula:—



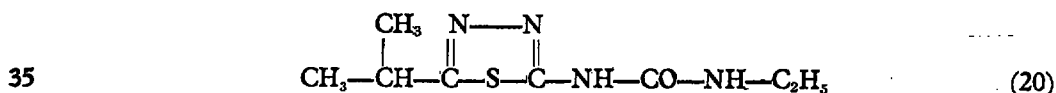
10. The thiadiazole of the formula:—



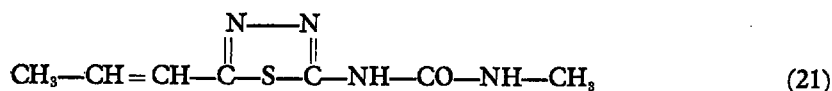
11. The thiadiazole of the formula:—



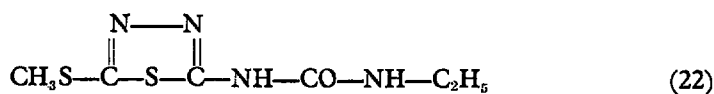
12. The thiadiazole of the formula:—



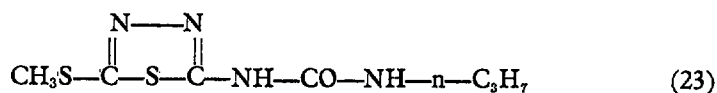
13. The thiadiazole of the formula:—



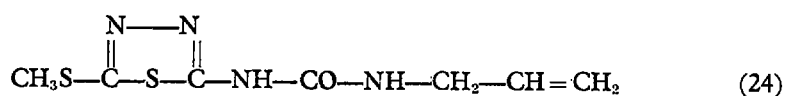
14. The thiadiazole of the formula:—



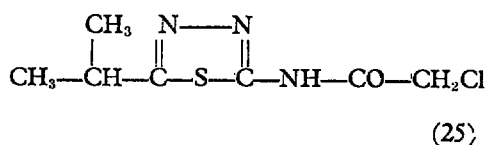
15. The thiadiazole of the formula:—



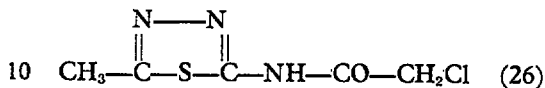
5 16. The thiadiazole of the formula:—



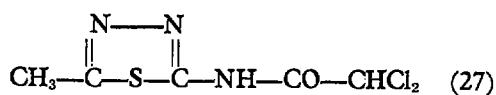
17. The thiadiazole of the formula:—



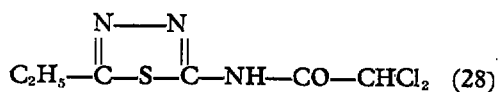
18. The thiadiazole of the formula:—



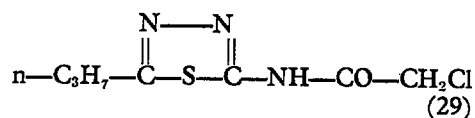
19. The thiadiazole of the formula:—



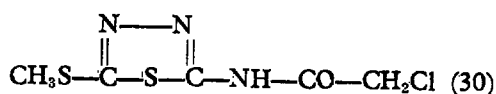
20. The thiadiazole of the formula:—



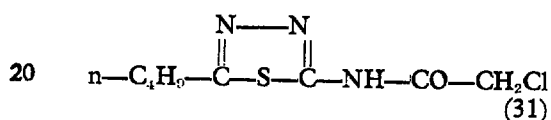
15 21. The thiadiazole of the formula:—



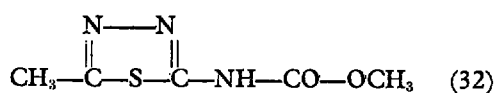
22. The thiadiazole of the formula:—



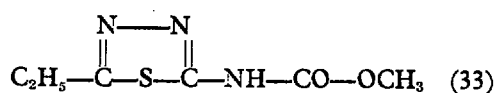
23. The thiadiazole of the formula:—



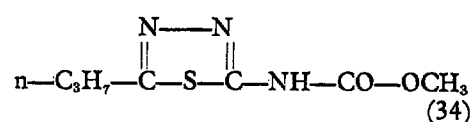
24. The thiadiazole of the formula:—



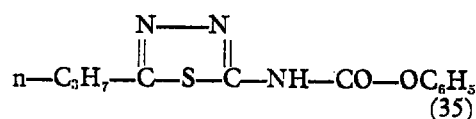
25. The thiadiazole of the formula:—



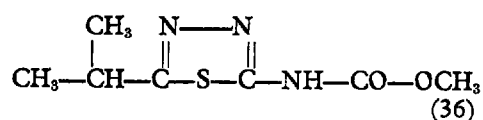
26. The thiadiazole of the formula:—



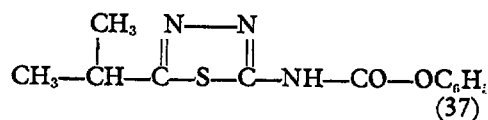
27. The thiadiazole of the formula:—



28. The thiadiazole of the formula:—

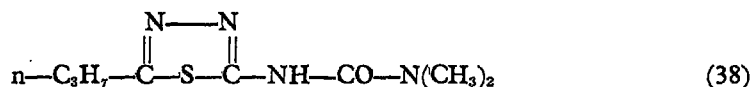


29. The thiadiazole of the formula:—

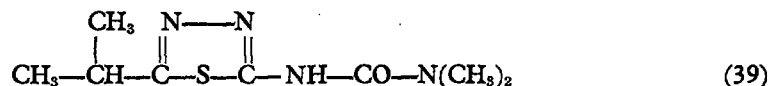




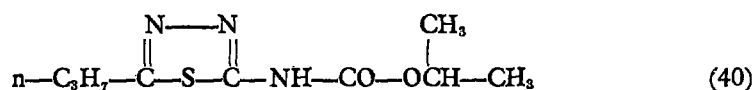
30. The thiadiazole of the formula:—



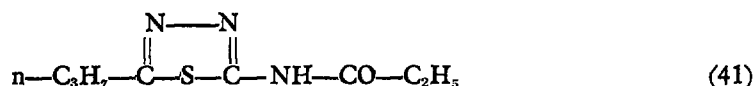
31. The thiadiazole of the formula:—



5 32. The thiadiazole of the formula:—



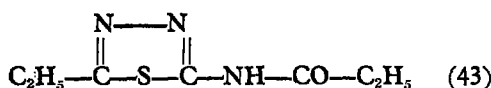
33. The thiadiazole of the formula:—



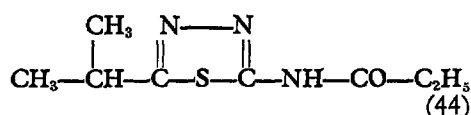
34. The thiadiazole of the formula:—



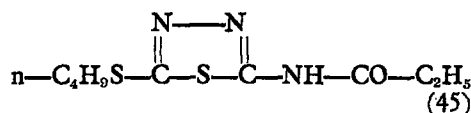
35. The thiadiazole of the formula:—



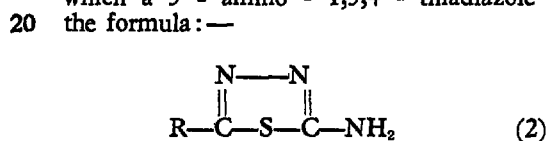
36. The thiadiazole of the formula:—



37. The thiadiazole of the formula:—

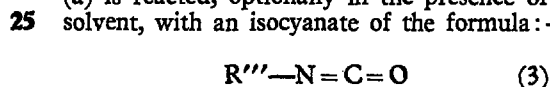


38. A process for the production of thiadiazoles according to any of claims 1 to 37 in which a 5 - amino - 1,3,4 - thiadiazole of the formula:—



in which

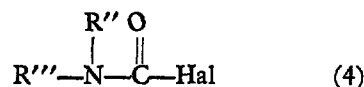
R has the same meaning as in claim 1
(a) is reacted, optionally in the presence of a solvent, with an isocyanate of the formula:—



in which

R''' has the same meaning as in claim 1, or (b) is reacted, in the presence of an acid binder, with an acid halide of the formula:—

30



in which

R'' and R''' have the same meaning as in claim 1, and Hal is halogen, or

(c) is reacted, in the presence of an acid binder, with an acid halide of the formula:—

35

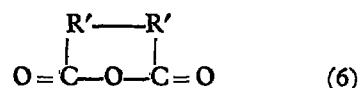


in which

R' has the same meaning as in claim 1, with the proviso that it is not —NR''R''', and Hal is halogen, or

40

(d) is reacted with an acid anhydride of the formula:—



in which

R' has the same meaning as in claim 1, with the proviso that it is not —NR''R'''.

45

39. A process according to claim 38 (a) in which the isocyanate is methyl isocyanate, ethyl isocyanate or isopropyl isocyanate.

50

40. A process according to claim 38(b) or 38(c) in which the acid chloride is dimethylcarbamic acid chloride, propionic acid chloride, monochloroacetic acid chloride, dichloroacetyl

- chloride or chloroformic acid methyl ester.
41. A process according to any of claims 38 to 40 in which the reaction is carried out at 0° to 140°C.
- 5 42. A process according to claim 41 in which the reaction is carried out at 10° to 120°C.
43. A process according to any of claims 38 to 42 in which the reaction is carried out in the presence of an inert solvent.
- 10 44. A process for the production of thiadiazoles according to claim 1 substantially as hereinbefore described in any of Examples 1 to 4.
45. Thiadiazoles whenever produced by a process according to any of claims 38 to 44.
- 15 46. A herbicidal composition containing as active ingredient a thiadiazole according to any of claims 1 to 37 or 45 in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.
- 20 47. A composition according to claim 46 containing from 0.1 to 95 per cent by weight, of the active compound.
- 25 48. A method of combating weeds which comprises applying to the weeds or to a weed habitat a thiadiazole according to any of claims 1 to 37 or 45 alone or in the form of a composition containing as active ingredient a thiadiazole according to any of claims 1 to 37 or 45 in admixture with a solid or liquid diluent or carrier.
- 30 49. A method according to claim 48 in which a composition is used containing from 0.01 to 5% of the active compound, by weight.
- 35 50. A method according to claim 49 in which a composition is used containing from 0.25 to 1% of the active compound, by weight.
51. A method according to any claims 48 to 50 in which the thiadiazole is applied to an area containing weeds in an amount of 1 to 50 kg per hectare.
- 40 52. A method according to any claims 48 to 51 in which the thiadiazole is one of those hereinbefore mentioned in Example A or B.
- 45 53. A method of providing a harvested crop which comprises applying a compound according to any claims 1 to 37 or 45 to the area of cultivation of the crop, whereby the latter is protected from damage by weeds, and harvesting the crop.
- 50 54. A method of defoliating plants which comprises applying to the plants a thiadiazole according to any of claims 1 to 37 or 45 alone or in admixture with a solid or liquid diluent or carrier whereby the leaves of the plants are caused to fall off or die.
- 55

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.



* C L M S *