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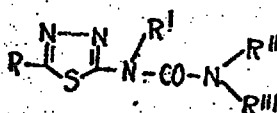
(71) We, BAYER AKTIENGESSELLSCHAFT, formerly known as Farbenfabriken Bayer Aktiengesellschaft, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed,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

The present invention relates to certain new 1,3,4-thiadiazolyl-(5)-ureas, to a process for their production and to their use as herbicides.

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

The present invention provides 1,3,4-thiadiazolyl-(5)-ureas of the formula

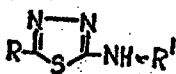
(a) a 5-amino-1,3,4-thiadiazole of the formula



in which

- R stands for hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, alkylmercapto, alkenylmercapto, alkynylmercapto, aralkylmercapto (the aryl radical of which may be substituted by chlorine or nitro), alkylsulphoxyl, alkylsulphonyl, aralkylsulphoxyl, aralkylsulphonyl, alkyloxy or $R^{IV}CO(CH_2)_nS-$ (in which R^{IV} stands for hydroxy, alkoxy, amino, alkylamino or arylamino (which may be substituted by chlorine), and
- n stands for 1, 2, 3 or 4),
- R' stands for alkyl,
- R'' stands for hydrogen or alkyl, and
- R''' stands for alkyl.

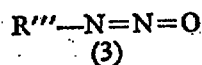
The present invention provides a process for the production of compounds according to the formula (1) in which



(2)

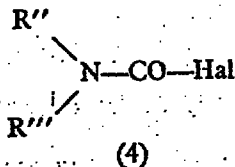
in which

R and R' have the meanings stated above
is reacted with an isocyanate of the formula



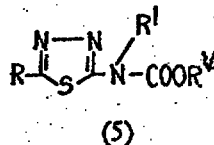
in which

- 5 R''' has the meaning stated above, or
(b) a compound of the formula (2) is reacted, in the presence of an acid-binding agent,
with an acid chloride of the formula



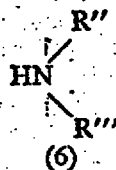
in which

- 10 R'' and R''' have the meanings stated above, and
Hal stands for halogen, or
(c) a urethane of the formula



in which

- 15 R and R' have the meaning stated above, and
R^v stands for methyl or phenyl
is reacted, at elevated temperature, with an amine of the formula

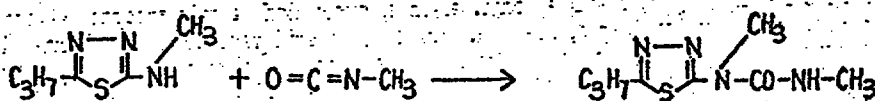


in which

- 20 R'' and R''' have the meaning stated above.

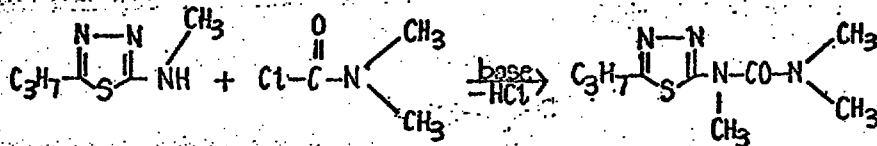
It is decidedly surprising that the new 1,3,4-thiadiazoles exhibit a stronger herbicidal activity and, in particular, better selective herbicidal properties, than the previously known thiazoles.

If 2-propyl-5-methylamino-1,3,4-thiadiazole and methylisocyanate are used as starting materials, the reaction course according to process variant (a) can be represented by the following formula scheme:



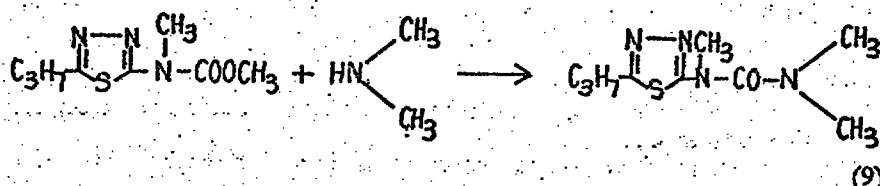
(7)

If dimethylcarbamic acid chloride is used for reaction with the same thiadiazole, the reaction course of the process variant (b) can be represented by the following formula scheme:



(8)

The process variant (c) proceeds in an analogous manner:



The thiadiazoles used as starting materials are defined by the formula (2) stated above. In this formula and in Formula (1), R stands preferably for hydrogen, alkyl, alkenyl, alkynyl with, in each case, up to 4 carbon atoms; cycloalkyl with 5 or 6 carbon atoms; alkoxy with 1 to 4 carbon atoms; alkylmercapto, alkenylmercapto and alkynylmercapto with, in each case, up to 4 carbon atoms; phenylalkylmercapto with 1 or 2 carbon atoms in the alkylene group and chlorine and/or nitro groups on the phenyl; alkoxysulphoxyl or alkylsulphonyl with 1 to 4 carbon atoms; or phenylalkylsulphoxyl or phenylalkylsulphonyl with 1 or 2 carbon atoms in the alkylene group. R' stands preferably for alkyl with 1 to 4 carbon atoms.

Examples of the alkylaminothiadiazoles to be used according to the invention include: 2-propyl-5-methylamino-1,3,4-thiadiazole; 2-isopropyl-5-methylamino-1,3,4-thiadiazole; 2-ethylmercapto-5-ethylamino-1,3,4-thiadiazole; 2-propylmercapto-5-ethylamino-1,3,4-thiadiazole; 2-ethylmercapto-5-methylamino-1,3,4-thiadiazole; 2-butylmercapto-5-methylamino-1,3,4-thiadiazole and 2-allylmercapto-5-methylamino-1,3,4-thiadiazole.

Some of the compounds of the formula (2) are already known. The still new thiadiazoles can be prepared in the same manner as the already known ones, for example by reaction of the appropriate 1-acylthiosemicarbazides with agents which split off water, such as acetic anhydride (Chemische Berichte 29, 2511 (1896)).

The isocyanates used as starting materials are defined by the formula (3) stated above. In Formula (3), R''' stands preferably for alkyl with 1 to 3 carbon atoms. As examples, methylisocyanate, ethylisocyanate and isopropylisocyanate are mentioned.

The acid chlorides used as starting materials are defined by the formula (4) stated above. In Formula (4) and in Formula (1), R'' stands preferably for hydrogen or alkyl with 1 to 3 carbon atoms and R''' for alkyl with 1 to 3 carbon atoms. As an example, dimethylcarbamic acid chloride is mentioned.

The urethanes used as starting materials are defined by the formula (5) stated above. R and R' have the preferred meaning stated above.

The amines used as starting materials are defined by the formula (6) stated above. R'' and R''' have the preferred meaning stated above for Formula (4).

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

In the following, further details for the carrying out of the process are given:

The process of the invention is preferably effected in the presence of a solvent (which term includes mere diluents); all inert organic solvents are suitable. The 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 acetate, and acetonitrile and dimethyl formamide.

As the acid-binding agent, any customary acid-binder can be used. The preferred acid-binding agents include alkali metal hydroxides, alkali metal carbonates and tertiary amines. Particularly suitable are sodium hydroxide, sodium carbonate, triethylamine and pyridine.

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

When carrying out the process according to the invention, approximately equimolar amounts of starting materials are generally used. The working up of the reaction mixture is effected in customary manner.

The active compounds according to the invention exhibit strong herbicidal properties and can therefore be used 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*), smallflower Galinsoga (*Galinsoga*), fathen (*Chenopodium*), stinging nettle (*Urtica*), groundsel (*Senecio*), cotton (*Gossypium*), beets. (*Beta*), carrots (*Daucus*), beans (*Phaseolus*),

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 are particularly well suited for selective weed control in cereals, cotton and carrots.

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 dimethyl 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 from 0.5 to 90, per cent by weight of active compound.

The active compounds may be used as such or 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 before or after emergence of the plants.

When the active compounds are used according to the post-emergence and the pre-emergence process, the amount applied can be varied within fairly wide ranges. In general, the amount is from 1 to 50 kg of active compounds per hectare, preferably from 2 to 20.

The active compounds also show a bactericidal effectiveness and can therefore be used for example in industrial disinfection.

The present invention also provides a herbicidal composition containing as active ingredient a 1,3,4-thiadiazolyl-(5)-urea of the present invention in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The present invention also provides a method of combating weeds which comprises applying to the weeds or a weed habitat a 1,3,4-thiadiazolyl-(5)-urea of the present invention alone or in the form of a composition containing as active ingredient a 1,3,4-thiadiazolyl-(5)-urea of the present invention in admixture with a solid or liquid diluent or carrier.

The present invention also provides crops protected from damage by weeds by being grown in areas in which immediately prior to and/or during the time of the growing a 1,3,4-thiadiazolyl-(5)-urea of the present invention was applied alone or in admixture with a solid or liquid diluent or carrier.

The excellent herbicidal activity of the compounds of the present invention is illustrated in the following Examples.

Example A

Pre-emergence test

Solvent: 5 parts by weight acetone

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.

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

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Pre-emergence test

Active compound	Active compound applied kg/hectare	<i>Echinochloa</i>	<i>Chenopodium</i>	<i>Stellaria</i>	<i>Galinsoga</i>	<i>Marricaria</i>	Oats	Cotton	Wheat	Maize
$\text{CH}_3-\text{C}(\text{N})=\text{S}-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3$ (known)	10 5 2.5	4 3 2	5 4 2-3	— — —	— — —	— — —	3-4 3 2	3 1 0	4 3 1	— — —
$\text{C}_2\text{H}_5-\text{S}-\text{C}(\text{N}=\text{N}-\text{C}_2\text{H}_5)=\text{N}-\text{CO}-\text{NH}-\text{CH}_3$ (17)	10 5 2.5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 4	5 5 4	5 4-5 4	5 5 4
$\text{C}_3\text{H}_7-\text{S}-\text{C}(\text{N}=\text{N}-\text{C}_2\text{H}_5)=\text{N}-\text{CO}-\text{NH}-\text{CH}_3$ (19)	10 5 2.5	5 5 4	5 5 5	5 5 4-5	5 5 5	5 5 5	3 2 1	2 1 0	2 1 0	4 3 2
$i-\text{C}_3\text{H}_7-\text{S}-\text{C}(\text{N}=\text{N}-\text{C}_2\text{H}_5)=\text{N}-\text{CO}-\text{NH}-\text{CH}_3$ (21)	10 5 2.5	4 4 3	5 4-5 4	5 5 4	5 5 5	5 5 4-5	4 4 3	5 4 4	3 1 0	3-4 3 2
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{S}-\text{C}(\text{N}=\text{N}-\text{C}_2\text{H}_5)=\text{N}-\text{CO}-\text{NH}-\text{CH}_3$ (25)	10 5 2.5	4 4 3	5 4-5 4	5 5 5	5 5 5	5 5 5	4 3 2	4 3 2	3 1 0	2 0 0

TABLE A (Continued)

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Pre-emergence test

Active compound	Active compound applied kg/hectare	Sinapis	Echinochloa	Chenopodium	Stellaria	Galinsoga	Marricaria	Oats	Cotton	Wheat	Maize
$\text{C}_3\text{H}_7-\text{S}-\text{N}=\text{N}-\text{CH}_3$ (18)	10 5 2.5	5 5 4	5 5 4-5	5 5 5	5 5 3	5 5 5	5 5 4-5	5 5 4	5 4-5 4	5 4 3	5 4 3
$\text{C}_4\text{H}_9-\text{S}-\text{N}=\text{N}-\text{CH}_3$ (22)	10 5 2.5	5 4 3	4-5 4 3	5 5 5	5 5 4	5 5 3-4	5 5 5	4 3 2	3 3 2	1-2 0 0	2 1 0
$\text{CH}_3-\text{C}-\text{CH}_2-\text{S}-\text{N}=\text{N}-\text{CH}_3$ (26)	10 5 2.5	5 4-5 4	5 5 4	5 5 5	5 5 4	5 5 4	5 5 4	4-5 3 4	3 2 0	3 2 1	3 1 0
$\text{C}_3\text{H}_7-\text{S}-\text{N}=\text{N}-\text{CH}_3$ (11)	10 5 2.5	5 5 3	4-5 4-5 3	5 5 4-5	5 5 4	5 5 4	5 5 5	4 3 2	3 2 2	2 1 0	2 0 0
$\text{i-C}_3\text{H}_7-\text{S}-\text{N}=\text{N}-\text{CH}_3$ (10)	10 5 2.5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 4-5	4 3 3	5 4 4	5 4 3
$\text{i-C}_3\text{H}_7-\text{S}-\text{N}=\text{N}-\text{CH}_3$ (13)	10 5 2.5	4 3 3	5 4 4	5 5 5	5 4-5 3	5 5 4	5 5 4	5 4 4	2 1 0	4 3 3	3 1-2 0

TABLE A (Continued)

Active compound	Active compound applied kg/hectare	Sina- pis	Echino- chloa	Cheno- podium	Stel- laria	Galin- soga	Marri- caria	Oats	Cotton	Wheat	Maize
$\text{CH}_3\text{SO}_2-\text{N}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_3$	10	5	5	5	5	5	5	3	3	4	3
	5	5	5	5	5	5	5	2	1-2	3	2
	2.5	4	5	5	5	5	5	0	0	2	1
$\text{CH}_3\text{SO}_2-\text{N}(\text{C}_2\text{H}_5)-\text{CO}-\text{NH}-\text{CH}_3$	10	5	5	5	5	5	5	5	5	5	5
	5	5	5	5	5	5	5	5	5	4-5	5
	2.5	5	5	5	5	5	4	4	4	4-5	4-5
$\text{C}_2\text{H}_5-\text{SO}_2-\text{N}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_3$	10	5	5	5	5	5	5	5	5	5	5
	5	5	5	5	5	5	5	5	5	5	5
	2.5	5	5	5	5	5	5	5	5	5	5
$\text{C}_3\text{H}_7-\text{SO}_2-\text{N}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_3$	10	5	5	5	5	5	5	3	3	2	5
	5	5	5	5	5	5	5	2	2	1	4
	2.5	4	5	5	5	5	5	1	1	0	2-3
$i\text{-C}_3\text{H}_7-\text{SO}_2-\text{N}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_3$	10	5	5	5	5	5	5	5	5	4-5	5
	5	5	5	5	5	5	5	4-5	4	4	4
	2.5	5	4-5	4	5	5	4-5	4-5	3	4	4

Example B

Post-emergence test

Solvent: 5 parts by weight acetone

Emulsifier: 1 part by weight alkylaryl polyglycol ether

5 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. 5

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. After three weeks, the degree of damage to the plants is determined and characterised by the values 0—5, which have the following meaning: 10

- 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

15 The active compounds, their concentrations and the results obtained can be seen from the following Table B: 20

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TABLE B

Post-emergence test

Active compound	Active compound applied kg/hectare	<i>Echinochloa</i>	<i>Chenopodium</i>	<i>Sinapis</i>	<i>Galinsoga</i>	<i>Stellaria</i>	<i>Marricaria</i>	Oats	Cotton	Wheat	Carrots
$\text{CH}_3-\text{N}(\text{S})-\text{NH}-\text{CO}-\text{NH}-\text{CH}_3$	4 2 1 (58)	4 3 1	5 4-5 3	5 4-5 4	5 4-5 3	4-5 3 2	— — —	1-2 1 0	2-3 2 0	1-2 1 0	3 1 0
— (known)											
$\text{C}_2\text{H}_5-\text{S}-\text{N}(\text{N})-\text{N}-\text{CO}-\text{NH}-\text{CH}_3$	4 2 1 (17)	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 4-5	5 5 5	5 4-5 4	5 5 5
$\text{C}_3\text{H}_7-\text{S}-\text{N}(\text{N})-\text{N}-\text{CO}-\text{NH}-\text{CH}_3$	4 2 1 (19)	5 5 4-5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 4	5 5 4	5 5 5	5 5 3-4	5 4 3
$i-\text{C}_3\text{H}_7-\text{S}-\text{N}(\text{N})-\text{N}-\text{CO}-\text{NH}-\text{CH}_3$	2 1 0.5 (21)	5 4 3-4	5 4-5 4	5 5 5	5 4-5 4	5 4 3	5 4-5 4	3 1 0	4 3 3	4 2 0	2 0 0
$\text{C}_2\text{H}_5-\text{S}-\text{N}(\text{N})-\text{N}-\text{CO}-\text{NH}-\text{CH}_3$	2 1 0.5 (16)	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 4-5 3	5 5 5	4-5 3 3	5 5 5

TABLE B (Continued)

Post-emergence test

Active compound	Active compound applied kg/hectare	<i>Echinochloa</i>	<i>Chenopodium</i>	<i>Sinapis</i>	<i>Galinsoga</i>	<i>Stellaria</i>	<i>Urtica</i>	<i>Matri-caria</i>	Oats	Cotton	Wheat	Carrots
<chem>Cc1ccc(cc1)S(=O)(=O)N(C)C(=O)N(C)C</chem> (22)	2 1 0.5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	4 2 1	5 5 4	2 1 0	5 5 5
<chem>Cc1ccc(cc1)S(=O)(=O)N(C)C(=O)N(C)C</chem> (24)	2 1 0.5	5 4-5 3	5 4-5 4-5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 4	5 4 4	5 4-5 4-5	2 0 0	5 5 5
<chem>Cc1ccc(cc1)S(=O)(=O)N(C)C(=O)N(C)C</chem> (14)	2 1 0.5	5 4 4	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	2 1 0	5 5 4	5 4 2	5 4-5 4-5
<chem>Cc1ccc(cc1)S(=O)(=O)N(C)C(=O)N(C)C</chem> (10)	2 1 0.5	5 5 5	5 5 5	5 5 5	5 5 4	5 5 5	5 5 5	5 4-5 3	5 4 4	5 5 5	5 5 4-5	3 1 1

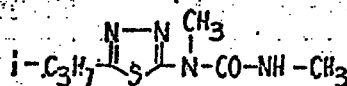
TABLE B (Continued)

Post-emergence test

Active compound	Active compound applied kg/hectare	<i>Echino- chloa</i>	<i>Cheno- podium</i>	<i>Sina- pis</i>	<i>Galini- soga</i>	<i>Stel- laria</i>	<i>Urutica caria</i>	Oats	Cotton	Wheat	Carrots
$\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CO}-\text{NH}-\text{CH}_3$	(32)	4 2 1	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 5 5
$\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CO}-\text{NH}-\text{CH}_3$	(33)	4 2 1	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 4-5 4	5 5 5	4 4 3	5 5 5
$\text{C}_2\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CO}-\text{NH}-\text{CH}_3$	(34)	4 2 1	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 4-5 5	5 5 5	4-5 4 3	5 5 5
$\text{C}_6\text{H}_7\text{SO}_2\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CO}-\text{NH}-\text{CH}_3$	(36)	4 2 1	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	4-5 4-5 3	5 5 5	4-5 4 3	5 5 5
$i\text{-C}_3\text{H}_7\text{SO}_2\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CO}-\text{NH}-\text{CH}_3$	(37)	4 2 1	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 4	5 5 5	4-5 4 4	5 5 5
$\text{C}_6\text{H}_9\text{SO}_2\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CO}-\text{NH}-\text{CH}_3$	(40)	4 2 1	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	4-5 3 1	5 5 5	2-3 1 0	5 5 5

The process of the present invention is illustrated in the following Example.

Example 1



7.2 g (0.126 mole) methylisocyanate are added dropwise to 19.7 g (0.126 mole) 2-isopropyl-5-methylamino-1,3,4-thiadiazole in 100 ml ethyl acetate. After subsidence of the heat effect, heating under reflux is continued for a further 4 hours. After the solvent has been distilled off, the crude N-(2-isopropyl-1,3,4-thiadiazolyl)-N,N'-dimethylurea is recrystallised from petroleum ether/acetone. m.p. 112°.

In analogous manner, the further ureas of the formula (1) mentioned in the

TABLE

Compound No.	R	R'	R''	R'''	m.p.
11	C ₃ H ₇	CH ₃	H	CH ₃	105°
12	C ₃ H ₇	C ₂ H ₅	H	CH ₃	98°
13	i-C ₃ H ₇	C ₂ H ₅	H	CH ₃	70°
14	CH ₃ S	CH ₃	H	CH ₃	163°
15	CH ₃ S	C ₂ H ₅	H	CH ₃	134°
16	C ₂ H ₅ S	CH ₃	H	CH ₃	84°
17	C ₂ H ₅ S	C ₂ H ₅	H	CH ₃	77°
18	C ₃ H ₇ S	CH ₃	H	CH ₃	85°
19	C ₃ H ₇ S	C ₂ H ₅	H	CH ₃	90°
20	i-C ₃ H ₇ S	CH ₃	H	CH ₃	102°
21	i-C ₃ H ₇ S	C ₂ H ₅	H	CH ₃	81°
22	C ₄ H ₉ S	CH ₃	H	CH ₃	82°
23	C ₄ H ₉ S	C ₂ H ₅	H	CH ₃	77°
24	CH ₂ =CHCH ₂ S	CH ₃	H	CH ₃	60°
25	CH ₂ =CHCH ₂ S	C ₂ H ₅	H	CH ₃	88°
26	CH≡CCH ₂ S	CH ₃	H	CH ₃	136°
27	CH≡CCH ₂ S	C ₂ H ₅	H	CH ₃	104°
28	CH ₃ S	C ₃ H ₇	H	CH ₃	113°
29	CH ₃ S	iso-C ₃ H ₇	H	CH ₃	114°
30	CH ₃ S	C ₄ H ₉	H	CH ₃	122°
31	CH ₃ S	iso-C ₄ H ₉	H	CH ₃	128°

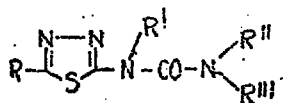
TABLE (Continued)

Compound No.	R	R'	R''	R'''	m.p.
32	CH ₃ SO ₂	CH ₃	H	CH ₃	184°
33	CH ₃ SO ₂	C ₂ H ₅	H	CH ₃	139°
34	C ₂ H ₅ SO ₂	CH ₃	H	CH ₃	157°
35	C ₂ H ₅ SO ₂	C ₂ H ₅	H	CH ₃	172°
36	C ₃ H ₇ SO ₂	CH ₃	H	CH ₃	146°
37	i-C ₃ H ₇ SO ₂	CH ₃	H	CH ₃	178°
38	i-C ₃ H ₇ SO ₂	C ₂ H ₅	H	CH ₃	141°
39	C ₃ H ₇ SO ₂	C ₂ H ₅	H	CH ₃	132°
40	C ₄ H ₉ SO ₂	CH ₃	H	CH ₃	129°
41	C ₄ H ₉ SO ₂	C ₂ H ₅	H	CH ₃	163°
42	C ₂ H ₅ S	C ₃ H ₇	H	CH ₃	oily
43	C ₂ H ₅ S	i-C ₃ H ₇	H	CH ₃	oily
44	C ₂ H ₅ S	i-C ₄ H ₉	H	CH ₃	73°
45	CH ₃ O	CH ₃	H	CH ₃	168°
46	CH ₃ O	C ₂ H ₅	H	CH ₃	140°
47	C ₃ H ₇ O	C ₂ H ₅	H	CH ₃	132°
48	i-C ₃ H ₇ O	C ₂ H ₅	H	CH ₃	134°
49	p-ClC ₆ H ₄ CH ₂ S	CH ₃	H	CH ₃	135°
50	p-ClC ₆ H ₄ CH ₂ S	C ₂ H ₅	H	CH ₃	136°
51	3,4-Cl ₂ C ₆ H ₃ CH ₂ S	CH ₃	H	CH ₃	94°
52	C ₆ H ₅ CH ₂ SO ₂	CH ₃	H	CH ₃	195°
53	HO ₂ CCH ₂ CH ₂ S	C ₂ H ₅	H	CH ₃	122°
54	H ₂ NCOCH ₂ CH ₂ S	CH ₃	H	CH ₃	174°
55	H ₂ NCOCH ₂ CH ₂ S	C ₂ H ₅	H	CH ₃	180°
56	p-ClC ₆ H ₄ NHCOCH ₂ CH ₂ S	CH ₃	H	CH ₃	224°
57	p-ClC ₆ H ₄ NHCOCH ₂ CH ₂ S	C ₂ H ₅	H	CH ₃	176°



WHAT WE CLAIM IS:—

1. 1,3,4-thiadiazolyl(5)-ureas of the general formula



(1)

in which

5 R stands for hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, alkylmercapto, alkenylmercapto, alkynylmercapto, aralkylmercapto (of which the aryl radical may be substituted by chlorine or nitro), alkylsulphoxyl, alkylsulphonyl, aralkylsulphoxyl, aralkylsulphonyl, alkylloxy or



10 (in which

R^{iv} stands for hydroxy, alkoxy, amino, alkylamino or arylamino, which may be substituted by chlorine, and

n stands for 1, 2, 3 or 4),

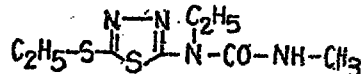
R' stands for alkyl,

15 R'' stands for hydrogen or alkyl, and

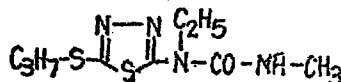
R''' stands for alkyl.

20 2. Compounds according to claims 1 in which R stands for hydrogen; alkyl, alkenyl, alkynyl, alkoxy, alkylmercapto, alkenylmercapto, alkynylmercapto, alkylsulphoxyl or alkylsulphonyl with up to 4 carbon atoms; cycloalkyl with 5 or 6 carbon atoms or phenylalkylmercapto (which may have chlorine or nitro on the phenyl), phenylalkylsulphoxyl or phenylalkylsulphonyl with 1 or 2 carbon atoms in the alkylene group; R' stands for alkyl with 1 to 4 carbon atoms; R'' stands for hydrogen or alkyl with 1 to 3 carbon atoms and R''' stands for alkyl with 1 to 3 carbon atoms.

3. The compound of the formula



4. The compound of the formula



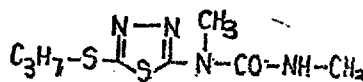
5. The compound of the formula



6. The compound of the formula



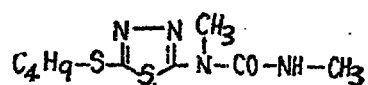
7. The compound of the formula



(18)

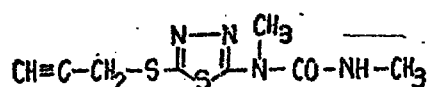


8. The compound of the formula



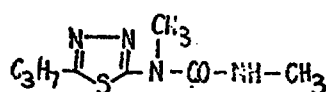
(22)

9. The compound of the formula



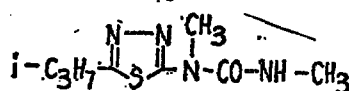
(26)

10. The compound of the formula



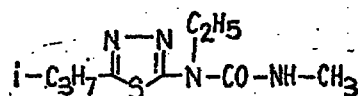
(11)

11. The compound of the formula



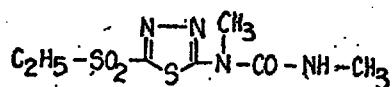
(10)

12. The compound of the formula



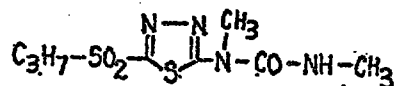
(13)

13. The compound of the formula



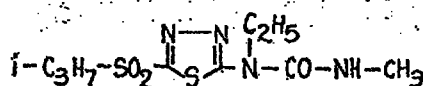
(34)

14. The compound of the formula



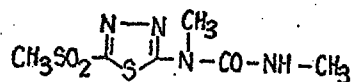
(36)

15. The compound of the formula



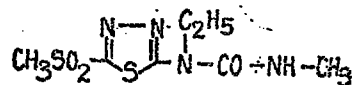
(38)

16. The compound of the formula



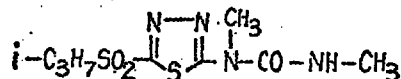


17. The compound of the formula



(33)

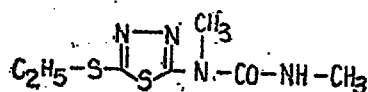
18. The compound of the formula



(37)

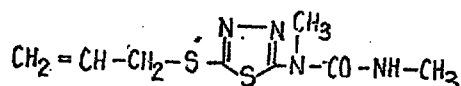
5

19. The compound of the formula



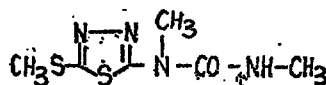
(16)

20. The compound of the formula



(24)

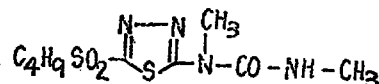
21. The compound of the formula



(14)

10

22. The compound of the formula



(40)

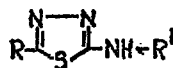
23. Any of the 1,3,4-thiadiazolyl-(5)-ureas according to claim 1 hereinbefore specifically mentioned.

15

24. A process for the production of 1,3,4-thiadiazolyl-(5)-ureas according to any of claims 1 to 23, in which

15

(a) a 5-amino-1,3,4-thiadiazole of the formula



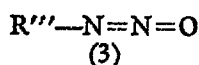
(2)

in which

20

R and R' have the meanings stated in claim 1 is reacted with an isocyanate of the formula

20



(3)

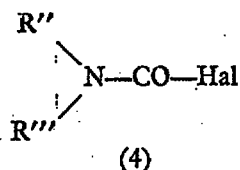
in which

R''' has the meaning stated in claim 1, or

(b) a compound of the formula (2) is reacted, in the presence of an acid-binding agent, with an acid chloride of the formula

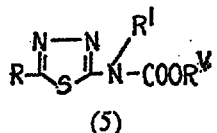
25

25



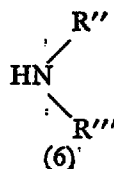
in which

R'' and R''' have the meanings stated in claim 1, and
Hal stands for halogen, or
(c) a urethane of the formula



in which

R and R' have the meaning stated in claim 1, and
R^V stands for methyl or phenyl
is reacted, at elevated temperatures, with an amine of the formula



in which

R'' and R''' have the meaning stated in claim 1.

25. A process according to claim 24 in which the reaction is effected in an inert solvent.

26. A process according to claim 24 or 25 in which the reaction is effected at a temperature of from 0° to 140°C.

27. A process according to claim 26 in which the reaction is effected at a temperature of from 10° to 120°C.

28. A process according to any of claims 24 to 27 in which the reagents are reacted in equimolar amounts.

29. A process according to claim 24 (b) or any of claims 25 to 28 when appendant to claim 24 (b) in which the acid-binding agent is an alkali metal hydroxide or carbonate or a tertiary amine.

30. A process according to claim 29 in which the acid-binding agent is sodium hydroxide, sodium carbonate, pyridine or triethylamine.

31. A process for the production of 1,3,4-thiadiazolyl-(5)-ureas according to claim 1 substantially as hereinbefore described in Example 1.

32. 1,3,4-thiadiazolyl-(5)-ureas according to claim 1 whenever produced by a process according to any of claims 24 to 31.

33. A herbicidal composition containing as active ingredient a compound according to any of claims 1 to 23 or 32 in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

34. A composition according to claim 33 containing from 0.1 to 95% of the active compound, by weight.

35. A composition according to claim 34 containing from 0.5 to 90% of the active compound, by weight.

36. A method of combating weeds which comprises applying to the weeds or a weed habitat a compound according to any of claims 1 to 23 or 32 alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 23 or 32 in admixture with a solid or liquid diluent or carrier.

37. A method according to claim 36 in which the active compound is applied to an area of agriculture in an amount of 1 to 50 kg per hectare.

38. A method according to claim 37 in which the active compound is applied in an amount of 2 to 20 kg per hectare.

39. A method according to any of claims 36 to 38 in which the active compound is one of those hereinbefore mentioned in Example A or Example B.

40. A method according to any of claims 36 to 39 in which the 1,3,4-thiadiazolyl-(5)-urea is applied to an area of cultivation of cereals, cotton or carrots.

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