

Singapore

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PATENT SPECIFICATION

(11) 1244 124

1244 1C4

NO DRAWINGS

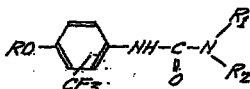
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 1Q9F1 1Q9L
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(54) UREA DERIVATIVES, THEIR MANUFACTURE AND USE AS HERBICIDES

(71) We, **FARBWERKE HOECHST AKTIENGESELLSCHAFT**, vormalig Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, 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 provides urea derivatives of the general formula



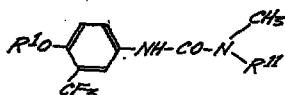
(I)
 in which R represents an alkyl group containing 1 to 4 carbon atoms, R₁ represents a hydrogen atom or an alkyl group containing 1 to 3 carbon atoms, and R₂ represents a methyl or a methoxy group.

The present invention also provides a process for the manufacture of the urea derivatives of the formula (I) which comprises reacting:

- 1) an alkoxy-trifluoromethyl-phenyl isocyanate or alkoxy-trifluoromethylcarbanilic acid chloride with
 - a) methylamine, dimethylamine, O-methyl- or O,N-dimethylhydroxylamine, or
 - b) hydroxylamine, I-methyl- or N-methylhydroxylamine, with subsequent alkylation or, if desired or required, dialkylation of the reaction product;
- or
- 2) an alkoxy-trifluoromethylaniline with
 - a) methyl isocyanate or dimethylcarbamic acid chloride, or
 - b) N,N-dimethyl- or methyl-methoxy-carbamic acid phenyl ester.

Compounds of the above formula (I) in which R₁ is an ethyl or propyl group when R₂ is a methyl group may be prepared by analogous methods.

The present invention especially provides urea derivatives of the following formula



(II)
 in which R' represents an alkyl group containing 2 to 4 carbon atoms and R'' represents a CH₃ or OCH₃ group, the said urea derivatives having an especially good selective herbicidal action.

The reactions may be represented, for example, by the following reaction schemes:

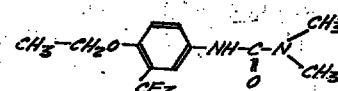
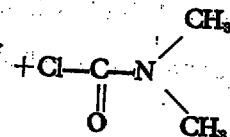
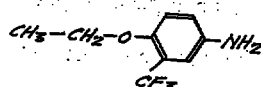
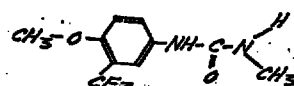
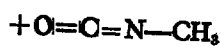
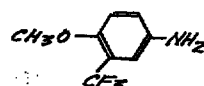
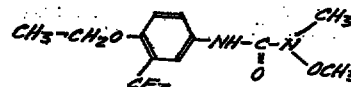
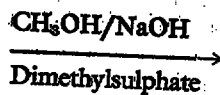
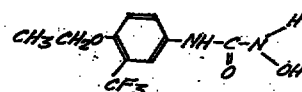
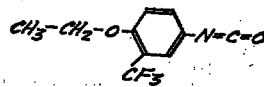
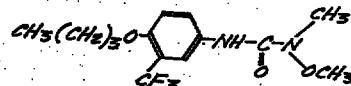
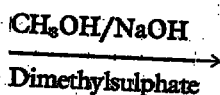
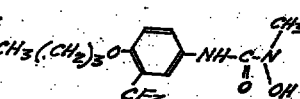
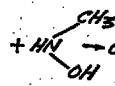
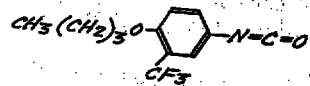
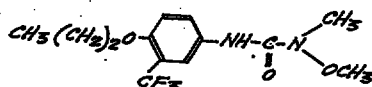
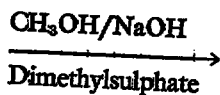
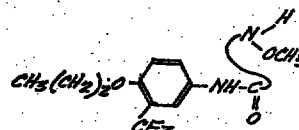
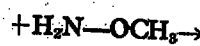
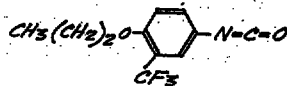
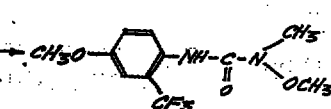
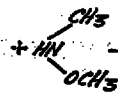
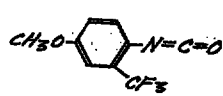
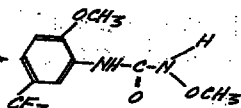
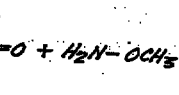
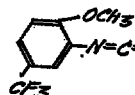
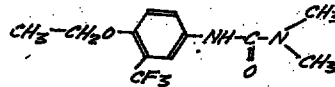
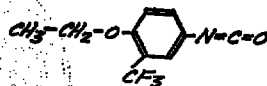
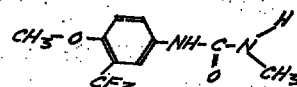
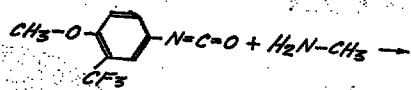
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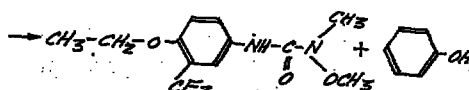
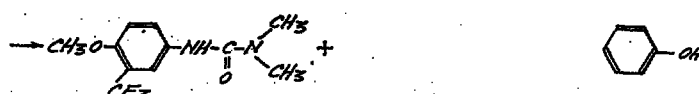
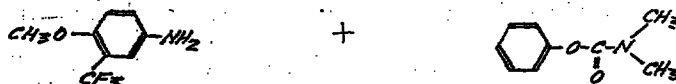
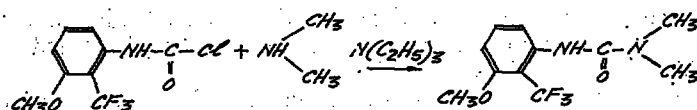
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The reaction of the alkoxy-trifluoromethylphenyl isocyanate or alkoxy-trifluoromethylcarbamic acid chloride with an amine or an alkylated hydroxylamine is advantageously carried out at a temperature of less than 80°C in the absence or presence of a diluent. Suitable diluents are, for example, benzene, toluene or dioxane.

The corresponding reactions with hydroxylamine are preferably carried out at a temperature of less than 40°C in a two-phase mixture of water and an organic solvent immiscible with water.

The alkylations are preferably carried out in aqueous-alkaline suspension or in a mixture of an aqueous alkali and an organic solvent. The alkali metal hydroxide solution and the alkylating agent are preferably added simultaneously, while controlling the pH value. Alternatively the urea may be placed first in the reaction vessel together with the alkylating agent in an organic solvent, and the alkali metal hydroxide solution may then be added, or in the case of compounds that are less sensitive towards alkali, the order of addition may be reversed. The reaction temperature naturally depends on the reactivity of the alkylating agent used and is within the range of from 10 to 90°C.

Suitable starting compounds for the above processes are, for example, 3-trifluoromethyl-4-methoxyphenyl isocyanate, 3-trifluoromethyl-6-methoxyphenyl isocyanate, 2-trifluoromethyl-4-methoxyphenyl isocyanate, 3-trifluoromethyl-4-ethoxyphenyl isocyanate, 3-trifluoromethyl-4-propoxyphenyl isocyanate and 3-trifluoromethyl-4-butoxyphenyl isocyanate.

Instead of the isocyanates, phenylcarbamic acid chlorides carrying the corresponding substituents may be used.

The isocyanates are obtained by phosgenation of a corresponding amine or a hydrochloride thereof. The alkylation in the above processes is carried out with a dialkyl sulphate, alkyl halide or alkyl-toluene sulphonate.

The novel compounds are obtained in good yields. They constitute, almost exclusively, crystalline compounds. They may be used as they are obtained, but may also be further purified by recrystallization from the usual organic solvents.

The novel compounds have a good action against undesired plant growth. They may be used in the form of wettable powders, emulsion concentrates, dusting powders or granules either alone or, if desired, in combination with other herbicides, soil insecticides or with fertilizers.

Thus, the present invention also provides herbicidal preparations, which comprise, as active ingredient, a compound of the general formula (I) or (II), together with a

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carrier, for example, a wetting or dispersing agent, an adhesive, a liquid or solid carrier material, a grinding agent or a granulating agent and, if desired, together with other herbicides, soil insecticides or fertilizers.

5 Wettable powders are preparations that can be uniformly dispersed in water and contain, besides an inert substance, a wetting agent, for example, polyoxethylated alkylphenols, polyoxethylated oleyl- or stearyl-amines, alkyl- or alkylphenyl sulphonates and dispersing agents, for example, the sodium salt of lignin-sulphonic acid, 2,2'-dinaphthylmethane-6,6'-disulphonic acid, dibutyl-naphthalene-sulphonic acid or sodium oleylmethyltaurine.

10 Emulsion concentrates are obtained by dissolving the active ingredient in an organic solvent, for example, butanol, cyclohexanone, dimethylformamide, xylene or aromatic hydrocarbons having a higher boiling point. To obtain good suspensions or emulsions in water, wetting agents as specified above are also added.

15 Dusting powders are obtained by grinding the active ingredients with finely divided, solid substances, for example, talc, natural clays, pyrophyllite or diatomaceous earth.

Granules can be prepared by atomizing the active ingredient on to an absorptive, granulated inert material, or by applying concentrates of the active ingredient to the surface of granulated inert materials with the aid of adhesives, for example, polyvinyl alcohol, the sodium salt of polyacrylic acid or mineral oils. Alternatively, suitable active ingredients may be made into granules, if desired in admixture with fertilizers, in the manner commonly used for the manufacture of granulated fertilizers.

The novel compounds of the invention can be used in combination with the following known herbicides, enumerated by way of example:

25	urea derivatives	linuron, chloroxuron, monolinuron, fluometuron, diuron	25
	triazine derivatives	simazin, atrazin, ametryne, prometryne, desmetryne, methoprotlyne	
	urazil derivatives	lenacil, bromacil	
	pyrazone derivatives	1-phenyl-4-amino-5-chloro-pyridazone (6) (POA)	
30	growth-promoting	2,4-dichloropheno-y-acetic acid (2,4-D), 4-chloro-2-	30
	preparations	methylphenoxy acetic acid (MCPA), 2,4,5-trichloro-phenoxy-acetic acid (2,4,5-T), 4-chloro-2-methylphenoxy-butyric acid (MCPB), 2,3,6-trichlorobenzoic acid (TBA)	
	carbamic acid derivatives	barban, phenmedipham, triallate, diallate, vernolate and 2-chloro-allyl-N,N-diethyl-dithiocarbamate (CDEC)	
35	dinitrophenol derivatives	dinitro-orthocresol (DNOC), dinitro-sec.-butylphenol (DNBP), dinosebacetate	35
	chlorinated aliphatic acids	trichloroacetic acid, dalapon	
	amides	diphenamide, N,N-diallyl-chloroacetamide (CDAA)	
40	dipyridilium compounds	paraquat, biquat, morfamquat	40
	anilides	N - (3,4 - dichlorophenyl) - methacrylamide (DCMA), propanil, solan (registered Trade Mark), monalide	
	nitriles	dichlobenil, ioxynil	
	other preparations	flurenol	

45 When the active ingredients according to the invention are mixed with fertilizers, preparations are obtained which simultaneously have a fertilizing and a herbicidal effect.

50 The novel compounds of the invention have a good action against weeds, for example, wild mustard, barnyard grass, chickweed, annual meadow grass and wild oat. They are superior to known urea derivatives, for example, N-3-chloro-4-methoxy-phenyl-N'-methyl-N'-methoxy urea, fluometuron and ametryne, in their sparing properties for a number of important cultivated plants, for example, cotton, wheat, barley, millet, carrot and leguminosae. Above all, novel compound N-[3-trifluoro-methyl-4-methoxyphenyl]-N',N'-dimethyl urea is distinguished by a particularly pronounced sparing property for cultivated plants.

55 The following Examples illustrate the invention, the parts being by weight:

Preparation Examples

EXAMPLE 1

60 3.5 grams (0.111 mol) of methylamine were added, while stirring, to 22 grams (0.1 mol) of 3-trifluoromethyl-4-methoxyphenyl isocyanate dissolved in 100 millilitres of absolute benzene, the temperature of the mixture increasing. After cooling, the

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formed crystals were suction-filtered and recrystallized from ethanol.

Yield: 24 grams

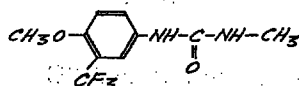
Melting point: 138 to 140°C

Analysis:

Calculated: 11.3 % N 23.0 % F

Found: 11.5 % N 22.6 % F

Molecular weight: 248



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$C_{10}H_{11}F_3N_2O_2$

EXAMPLE 2

5

6.3 grams (0.11 mol) of methyl isocyanate in 20 millilitres absolute benzene were added, while stirring, to 19 grams (0.1 mol) of 3-trifluoromethyl-4-methoxyaniline dissolved in 100 millilitres of absolute benzene. The mixture was heated for 1 hour at 50°C. After cooling, the precipitated reaction product was suction-filtered and recrystallized from ethanol.

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Yield: 23 grams

Melting point: 139 to 141°C

The mixed melting point with the product of Example 1 did not show a depression.

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EXAMPLE 3

15

6.3 grams (0.14 mol) of dimethylamine were added, while stirring, to 22 grams (0.1 mol) of 3-trifluoromethyl-4-methoxyphenyl isocyanate dissolved in 100 millilitres of absolute benzene. The crystals which formed were suction-filtered and recrystallized from carbon tetrachloride.

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Yield: 25 grams

Melting point: 119 to 121°C

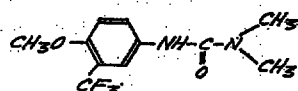
Analysis:

Calculated: 10.7 % N 21.8 % F

Found: 10.8 % N 21.5 % F

Molecular weight: 262

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$C_{11}H_{13}F_3N_2O_2$

EXAMPLE 4

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A solution of 14 grams (0.13 mol) of dimethylcarbamic acid chloride in 50 millilitres of absolute benzene was added at 40°C, while stirring, to a mixture of 25 grams (0.13 mol) of 3-trifluoromethyl-4-methoxyaniline, 11.3 grams (0.13 mol) of triethylamine and 100 millilitres of absolute benzene. The reaction mixture was kept at 40°C for 2 hours. After cooling, the crystalline reaction product was suction-filtered, washed with water until free from chlorine and then recrystallized from carbon tetrachloride.

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Yield: 24 grams

Melting point: 120 to 121°C

The mixed melting point with the product of Example 3 did not show a depression.

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EXAMPLE 5

35

5.3 grams (0.11 mol) of O-methylhydroxylamine were added dropwise, while stirring, to 22 grams (0.1 mol) of 3-trifluoro-4-methoxyphenyl isocyanate dissolved in 100 millilitres of absolute benzene. The batch was kept at 40°C for a further hour. After cooling, the crystalline reaction product was suction-filtered and recrystallized from benzene.

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Yield: 24 grams

Melting point: 105 to 107°C

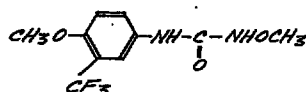
Analysis:

Calculated: 10.5 % N 21.6 % F

Found: 10.6 % N 22.0 % F

Molecular weight: 264

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$C_{10}H_{11}F_3N_2O_2$

EXAMPLE 6

6.8 grams (0.111 mol) of O,N-dimethylhydroxylamine were added dropwise, while stirring, to 22 grams (0.1 mol) of 3-trifluoromethyl-4-methoxyphenyl isocyanate dissolved in 100 millilitres of absolute benzene. The mixture was then heated under reflux for 30 minutes and the solvent was substantially distilled off. After cooling, the crystalline reaction product was suction-filtered and recrystallized from carbon tetrachloride.

Yield: 25 grams

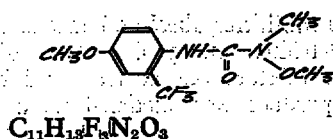
Melting point: 70 to 72°C

Analysis:

Calculated: 10.1 % N 20.5 % F

Found: 10.3 % N 20.1 % F

Molecular weight: 278



EXAMPLE 7

A solution of 33 grams (0.13 mol) of 3-trifluoromethyl-4-methoxyphenylcarbamic acid chloride in 50 millilitres of absolute benzene was added at 40°C, while stirring, to a mixture of 8 grams (0.13 mol) of O,N-dimethylhydroxylamine, 11.3 grams (0.13 mol) of triethylamine and 100 millilitres of absolute benzene. The reaction mixture was kept at 40°C for 2 hours. After cooling, the crystalline reaction product was suction-filtered, washed with water until free from chlorine and then recrystallized from carbon tetrachloride.

Yield: 31 grams

Melting point: 68 to 69°C

The mixed melting point with the product of Example 6 did not show a depression.

EXAMPLE 8

100 millilitres of methanol and 10 millilitres of sodium hydroxide solution of 33 % strength were added to 26.4 grams (0.1 mol) of N-[3-trifluoromethyl-4-methoxyphenyl]-N'-methoxy-urea (cf. Example 5). Into this mixture 14 grams (0.111 mol) of dimethyl sulphate were added dropwise, while cooling with icewater and stirring. The mixture was then heated for 1 hour at 30 to 35°C and diluted with an excess amount of water. The reaction product which precipitated was suction-filtered, washed with water and recrystallized from carbon tetrachloride.

Yield: 24 grams

Melting point: 68 to 70°C

The mixed melting point with the products of Examples 6 and 7 did not show a depression.

EXAMPLE 9

25 grams (0.1 mol) of N-[3-trifluoromethyl-4-methoxyphenyl]-N'-hydroxy-urea obtained from 3-trifluoromethyl-4-methoxyphenyl isocyanate and hydroxylamine in a manner analogous to that described in Example 6 were dissolved in 150 millilitres of methanol. 25 millilitres of a 10 N-sodium hydroxide solution and 32.5 grams (0.25 mol) of dimethyl sulphate were added simultaneously drop by drop at 20°C and a pH of 9 to 10, while stirring. The mixture was kept for 1 hour at 20°C for an after-reaction, and then diluted with ice-water, the precipitated reaction product was suction-filtered, washed with water and recrystallized from carbon tetrachloride.

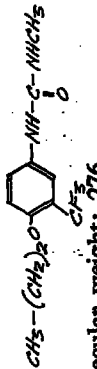
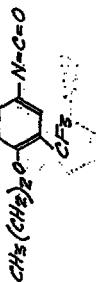
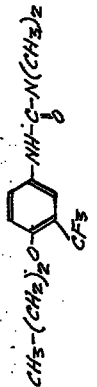
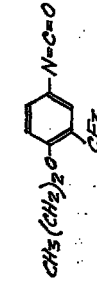
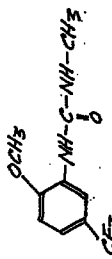
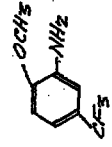
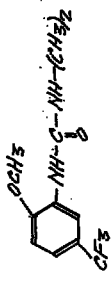
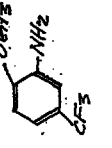
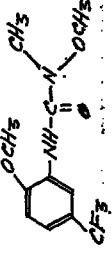
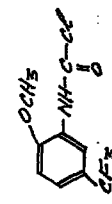
Yield: 23 grams

Melting point: 68 to 69°C

The mixed melting point with the products of Examples 6, 7 and 8 did not show a depression.

The compounds listed in the following Table were prepared in a manner analogous to the preceding Examples.

TABLE

Ex- ample	Final product	Pre- paration analo- gous to Example	Reactants	Melting point °C.	Analysis	
					calculated	found
10	 <chem>CH3-(CH2)2-O-C6H3(CF3)-NH-C(=O)-N(CH3)2</chem> Molecular weight: 276	1	 <chem>CH3-(CH2)2-O-C6H3(CF3)-N-C(=O)-O</chem> <chem>H2N-CH3</chem>	132-133	10.1% N 20.6% F	10.2% N 20.3% F
11	 <chem>CH3-(CH2)2-O-C6H3(CF3)-NH-C(=O)-N(CH3)2</chem> Molecular weight: 290	3	 <chem>CH3-(CH2)2-O-C6H3(CF3)-N-C(=O)-O</chem> <chem>HN(CH3)2</chem>	115-116	9.7% N 19.7% F	9.9% N 19.5% F
12	 <chem>CH3-(CH2)2-O-C6H3(CF3)-NH-C(=O)-N(CH3)2</chem> Molecular weight: 248	2	 <chem>O=C=N-CH3</chem>	160-161	11.3% N 23.0% F	11.5% 22.7% F
13	 <chem>CH3-(CH2)2-O-C6H3(CF3)-NH-C(=O)-N(CH3)2</chem> Molecular weight: 262	4	 <chem>Cl-C(=O)-N(CH3)2</chem>	99-101	10.7% N 21.8% F	10.6% N 21.4% F
14	 <chem>CH3-(CH2)2-O-C6H3(CF3)-NH-C(=O)-N(CH3)2</chem> Molecular weight: 278	7	 <chem>CH3</chem> <chem>HN</chem> <chem>OCH3</chem>	76-78	10.1% N 20.5% F	10.3% N 20.3% F

(14)

8

1,244,124

8

TABLE (Continued)

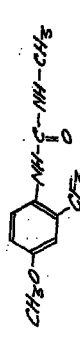
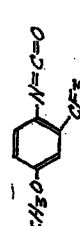
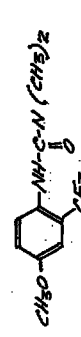
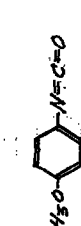
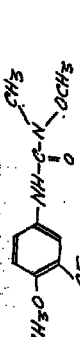
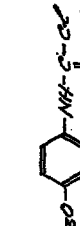
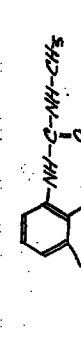
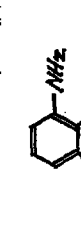
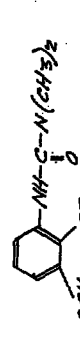
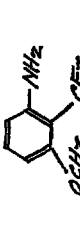
Ex- ample	Final product	Pre- paration analo- gous to Example	Reactants	Melting point °C.	Analysis	
					calculated	found
15	 Molecular weight: 248	1	 $\text{H}_2\text{N}-\text{CH}_3$	182—184	11.3% N 23.0% F	11.5% N 22.8% F
16	 Molecular weight: 262	3	 $\text{HN}(\text{CH}_3)_2$	134—136	10.7% N 21.8% F	10.7% N 21.4% F
17	 Molecular weight: 278	7	 CH_3 $\text{HN}-\text{OCH}_3$	oil	10.1% N 20.5% F	9.8% N 20.2% F
18	 Molecular weight: 248	2	 $\text{O}=\text{C}-\text{N}-\text{CH}_3$	189—190	11.3% N 23.0% F	11.5% N 22.8% F
19	 Molecular weight: 262	4	 $\text{Cl}-\text{C}(=\text{O})-\text{N}(\text{CH}_3)_2$	139—140	10.7% N 21.8% F	10.6% N 21.5% F

TABLE (Continued)

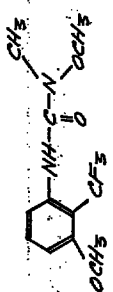
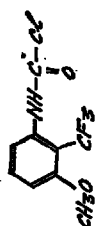
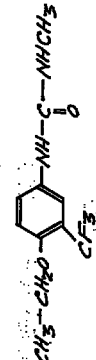
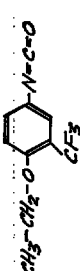
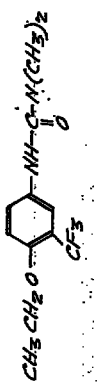
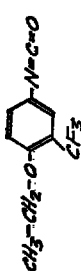
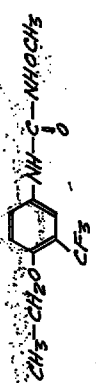
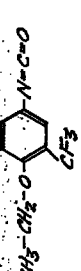
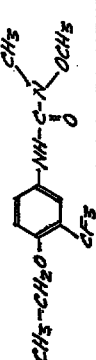
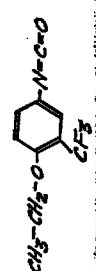
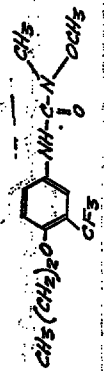
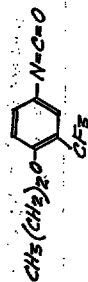
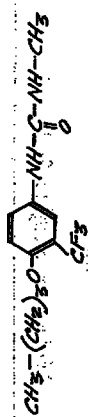
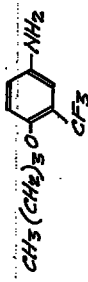
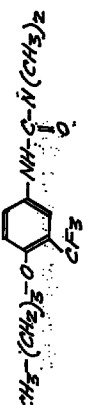
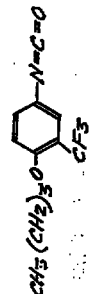
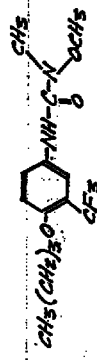
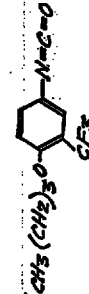
Ex-ample	Final product	Pre-paration analo- gous to Example	Reactants	Melting point °C.	Analysis	
					calculated	found
20	 Molecular weight: 278	7	 CH_3 $\text{HN}-\text{C}-\text{OCH}_3$	37—38	10.1% N 20.5% F	10.4% N 20.8% F
21	 Molecular weight: 262	1	 $\text{H}_2\text{N}-\text{CH}_3$	115—117	10.7% N 21.8% F	10.5% N 21.5% F
22	 Molecular weight: 276		 $\text{HN}(\text{CH}_3)_2$	120—122	10.1% N 20.6% F	10.3% N 21.0% F
23	 Molecular weight: 278	5	 $\text{H}_2\text{N}-\text{OCH}_3$	103—106	10.1% N 20.5% F	9.8% N 20.4% F
24	 Molecular weight: 292	9	 NH_2OH dimethyl sulphate	70—72	9.6% N 19.5% F	9.7% N 19.7% F

TABLE (Continued)

Ex-ample	Final product	Pre-paration analo-gous to Example	Reactants	Melting point °C.	Analysis	
					calculated	found
25	 Molecular weight: 306	8	 $\text{H}_2\text{N}-\text{OCH}_3$ dimethyl sulphate	oil	9.2% N 18.6% F	9.1% N 18.6% F
26	 Molecular weight: 290	2	 $\text{O}=\text{C}-\text{N}-\text{CH}_3$	116—118	9.7% N 19.7% F	9.9% N 19.4% F
27	 Molecular weight: 304	3	 $\text{HN}(\text{CH}_3)_2$	98—100	9.2% N 18.8% F	9.4% N 18.6% F
28	 Molecular weight: 320	9	 NH_2OH dimethyl sulphate	oil	8.8% N 17.8% F	8.8% N 17.5% F

EXAMPLE 29

A wettable powder which could easily be dispersed in water was obtained by mixing 80 parts N-[3-trifluoromethyl-4-methoxyphenyl]-N',N'-dimethyl-urea as active ingredient, 17 parts precipitated silicic acid as inert substance and 3 parts sodium oleylmethyltaurine as wetting and dispersing agent, and grinding the mixture in a disc attrition mill.

EXAMPLE 30

A dusting powder having good herbicidal properties was obtained by mixing 10 parts N-[3-trifluoromethyl-4-ethoxyphenyl]-N',N'-dimethyl-urea as active ingredient and 90 parts talc as inert substance and grinding the mixture in a cross beater mill.

EXAMPLE 31

An emulsion concentrate was obtained from 15 parts N-[3-trifluoromethyl-4-ethoxyphenyl]-N',N'-dimethyl-urea, 75 parts cyclohexanone as solvent and 10 parts nonyl(ethoxy)₁₀ phenol as emulsifier.

EXAMPLE 32

The weeds wild mustard (*Sinapis arvensis*) and barnyard grass (*Echinochloa crus-galli*) and the cultivated plant cotton (*Gossypium hirsutum*) were sown in pots. After the plants had emerged and developed two leaves, they were treated with wettable powder formulations suspended in water of the following preparations I=N-(3-trifluoromethyl-4-methoxyphenyl)-N',N'-dimethyl-urea and II=N-(3-trifluoromethyl-4-ethoxyphenyl)-N',N'-dimethyl-urea.

As comparative substance, a chemically similar known urea derivative, N-(3-chloro-4-methoxyphenyl)-N'-methyl-N'-methoxy-urea (cf. U.S. Patent 3,228,762), was used.

The evaluation after 4 weeks with a concentration of 1.25 kilograms of active compound per hectare gave the following result:—

Degree of damage in per cent

(100 = complete destruction, 0 = no damages)

wild mustard	I	95
	II	95
	comparative substance	95
barnyard grass	I	100
	II	100
	comparative substance	75
cotton	I	25
	II	0
	comparative substance	60

The herbicidal effect of the substances of the invention on the broad-leaved wild mustard was consequently approximately equal to that of the comparison substance, whereas the substances of the invention were clearly superior to the comparison substance in the case of the graminaceous barnyard grass. The substances in accordance with the invention did no or only little harm to the cotton plant whereas the comparative substance strongly burned the leaves.

EXAMPLE 33

	The weeds:	Sinapis arvensis
	wild mustard	Stellaria media
	chickweed	Echinochloa crus-galli
5	barnyard grass	Poa annua
	annual meadow grass	Eleusine indica
	and the cultivated plants:	Daucus carota
	carrot	Pisum sativum
10	pea	Vicia faba
	horse bean	Hordeum distichum
	barley	Triticum aestivum
	wheat	Sorghum vulgare
	sorghum millet	

where sown in boxes with humous sandy loam. The same day, the surface of the soil was sprayed with a wettable powder formulation suspended in water of preparation II=N-(3-trifluoromethyl-4-ethoxyphenyl)-N',N'-dimethyl-urea. As comparison substance the known urea product fluometuron=N-(3-trifluoromethylphenyl)-N',N'-dimethyl-urea was used. 0.6 kilogram active compound was used per hectare. An evaluation after 6 weeks gave the following result:

Degree of damage in per cent

	II	Comparison substance
<u>Weeds</u>		
wild mustard	100	95
chickweed	100	100
barnyard grass	95	95
annual meadow grass	100	100
Eleusine indica	100	90
<u>Cultivated Plants</u>		
carrot	0	75
pea	0	75
horse bean	10	55
barley	0	60
wheat	0	70
sorghum millet	0	70

The herbicidal effect of the substance of the invention was consequently approximately equal to that of the comparison substance. Whereas, however, the cultivated plants treated with the comparison substance showed pronounced or very pronounced phenomena of withering and more or less ceased to grow, the cultivated plants treated with the novel substance were not damaged or only little so.

EXAMPLE 34

Wild oat (*Avena fatua*) is a weed which may be annoying in spring grain and which is difficult to control because of its close botanical relationship to cereals. The following test shows that this problem can be solved with the urea herbicides of the

invention. Spring barley and spring wheat were sown in a field strongly infested with wild oat. On the day of sowing, the surface of the soil was sprayed, in plots each 10 m² large, with aqueous suspensions of the following substances:

II = N-(3-trifluoromethyl-4-ethoxyphenyl)-N',N'-dimethyl-urea

III = N-(3-trifluoromethyl-4-ethoxyphenyl)-N'-methyl-N'-methoxy-urea, and

IV = N-(3-trifluoromethyl-4-methoxyphenyl)-N'-methyl-N'-methoxyurea.

As comparison substance fluometuron and the triazine derivative 2-methyl-mercapto-4-ethylamino-6-tert-butyl-amino-s-triazine (AMETRYN) known as grain herbicide were used.

Two months after the treatment the following result was ascertained:

Concentration of active ingredient (kg/ha)	Preparation	Herbicidal action against		Damage to cultivated plants	
		wild oat	other weeds	barley	wheat
2 kg/ha	II	90—95%	75—100%	0	0
3 kg/ha	II	90—100%	80—100%	0	0
3 kg/ha	III	80—90%	70—90%	0	0
3 kg/ha	IV	80—90%	70—90%	slightly damaged	
2 kg/ha	fluometuron	90—95%	75—100%	very strongly damaged	
3 kg/ha	— „ —	90—100%	85—100%		
2 kg/ha	triazine derivative	0%	65—100%	0	0

Other weeds present were wild mustard (*Sinapis arvensis*), goose-foot (*Chenopodium album*), chickweed (*Stellaria media*), speedwell (*Veronica sp.*) and knot-grass (*Polygonum sp.*).

The above values show that 2 to 3 kilograms/hectare of the substances of the invention very strongly damaged and in some cases even destroyed the plants of wild oat, without having any effect on the barley and the wheat. The Table also shows that the compounds were also well effective against other weeds.

The chemically closely related preparation fluometuron used in the same concentrations had a similar effect on wild oat, but damaged the two species of grain so strongly that the plants showed phenomena of withering, were strongly retarded in growth and even died in some cases. On the other hand, the wild oat, like barley and wheat, was not injured at all by a typical grain herbicide as the above triazine derivative.

Contrary to other products, the preparations in accordance with the invention enable an effective control of wild oat in grain.

Test report

Spring wheat (*Triticum aestivum*), spring barley (*Hordeum distichum*), wild oat (*Avena fatua*) and various broad-leaved weeds (*Sinapis arvensis*, *Stellaria media*, *Galium aparine*, *Anthemis arvensis*, *Veronica arvensis* and *Polygonum persicaria*) were sown in boxes with humous sandy loam. On the same day, the surface of the soil was sprayed with aqueous suspensions of the following preparations:

V = N-3-trifluoromethyl-4-ethoxyphenyl-N'-methyl-urea (cf. Example 21), and

VI = N-3-trifluoromethyl-4-propoxyphenyl-N',N'-dimethyl-urea (cf. Example 11).

As comparison substance, fluometuron and the triazine derivative 2-methyl-mercapto-4-ethylamino-6-tert-butylamino-s-triazine were used.

The evaluation 5 weeks after the treatment with a concentration of 0.6 kilogram active ingredient per hectare gave the following result:

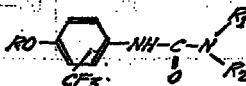
Degree of damage in per cent

	V	VI	Fluometuron	Triazine derivative
wheat	0	0	95	0
barley	0	10	95	0
Weeds				
wild oat	85	100	100	20
other weeds				
(mean value)	83	88	91	92

The above Table shows that all the preparations had a good to very good action against broad-leaved weeds. The substances of the invention moreover very strongly injured or even completely destroyed the wild oat while simultaneously sparing the cereals, whereas the comparison substances either spared the cereals as well as the wild oat (triazine derivative) or destroyed both the wild oat and the cereals.

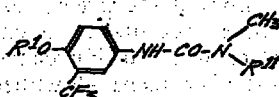
WHAT WE CLAIM IS:—

1. Compounds of the general formula



in which R represents an alkyl group containing 1 to 4 carbon atoms, R₁ represents a hydrogen atom or an alkyl group containing 1 to 3 carbon atoms and R₂ represents a methyl or methoxy group.

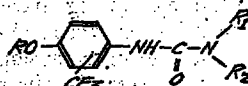
2. Compounds of the general formula



in which R' represents an alkyl group containing 2 to 4 carbon atoms and R'' represents a CH₃ or OCH₃ group.

3. Compounds as claimed in claim 1 or 2, obtainable substantially as described in any one of Examples 1 to 9 or with reference to the Table herein.

4. A process for the manufacture of urea derivatives of the general formula



in which R represents an alkyl group containing 1 to 4 carbon atoms, R₁ represents a hydrogen atom or an alkyl group containing 1 to 3 carbon atoms and R₂ represents a methyl or methoxy group, which comprises reacting:

- 1) as alkoxy-trifluoromethylphenyl isocyanate or alkoxy-trifluoromethylcarbanilic acid chloride with
 - a) methylamine, dimethylamine, O-methyl- or O,N-dimethylhydroxylamine, or

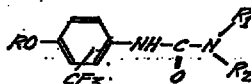
Degree of damage in per cent

	V	VI	Fluometuron	Triazine derivative
wheat	0	0	95	0
barley	0	10	95	0
<u>Weeds</u>				
wild oat	85	100	100	20
other weeds				
(mean value)	83	88	91	92

The above Table shows that all the preparations had a good to very good action against broad-leaved weeds. The substances of the invention moreover very strongly injured or even completely destroyed the wild oat while simultaneously sparing the cereals, whereas the comparison substances either spared the cereals as well as the wild oat (triazine derivative) or destroyed both the wild oat and the cereals.

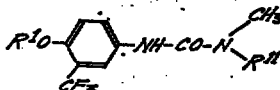
WHAT WE CLAIM IS:—

1. Compounds of the general formula



in which R represents an alkyl group containing 1 to 4 carbon atoms, R₁ represents a hydrogen atom or an alkyl group containing 1 to 3 carbon atoms and R₂ represents a methyl or methoxy group.

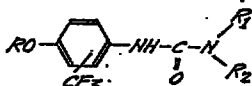
2. Compounds of the general formula



in which R' represents an alkyl group containing 2 to 4 carbon atoms and R'' represents a CH₃ or OCH₃ group.

3. Compounds as claimed in claim 1 or 2, obtainable substantially as described in any one of Examples 1 to 9 or with reference to the Table herein.

4. A process for the manufacture of urea derivatives of the general formula



in which R represents an alkyl group containing 1 to 4 carbon atoms, R₁ represents a hydrogen atoms or an alkyl group containing 1 to 3 carbon atoms and R₂ represents a methyl or methoxy group, which comprises reacting:

- 1) as alkoxy-trifluoromethylphenyl isocyanate or alkoxy-trifluoromethylcarbanilic acid chloride with
 - a) methylamine, dimethylamine, O-methyl- or O,N-dimethylhydroxylamine, or



b) hydroxylamine, O-methyl- or N-methyl-hydroxylamine, with subsequent alkylation or, if desired or required, dialkylation of the reaction product;

or

2) an alkoxy-trifluoromethylaniline with

a) methyl isocyanate or dimethylcarbamic acid chloride, or

b) N,N-dimethyl- or methyl-methoxy-carbamic acid phenyl ester.

5. A process as claimed in claim 4, wherein the reaction of the alkoxy-trifluoromethylphenyl isocyanate or alkoxy-trifluoromethylcarbamic acid chloride with an amine or an alkylated hydroxylamine is carried out at a temperature of less than 80°C in the absence or presence of a diluent.

6. A process as claimed in claim 5, wherein the diluent is benzene, toluene or dioxane.

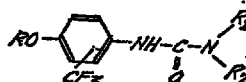
7. A process as claimed in claim 4, wherein the reaction of the alkoxy-trifluoromethylphenyl isocyanate or alkoxy-trifluoromethylcarbamic acid chloride with hydroxylamine is carried out at a temperature of less than 40°C in a two-phase mixture of water and an organic solvent immiscible with water.

8. A process as claimed in any one of claims 4 to 7, wherein the alkylation is carried out in an aqueous alkaline suspension or in a mixture of an aqueous alkali with an organic solvent.

9. A process as claimed in claim 8, wherein the alkylation is carried out at a temperature within the range of from 10 to 90°C.

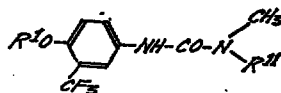
10. A process as claimed in claim 4, conducted substantially as described in any one of Examples 1 to 9, or with reference to the Table herein.

11. A herbicidal preparation which comprises as active ingredient a compound of the general formula



in which R represents an alkyl group containing 1 to 4 carbon atoms, R₁ represents a hydrogen atom or an alkyl group containing 1 to 3 carbon atoms and R₂ represents a methyl or methoxy group, together with a carrier and, if desired, a further biocidal active ingredient or a fertilizer.

12. A herbicidal preparation as claimed in Claim 11 containing as active ingredient a compound of the general formula



in which R' represents an alkyl group containing 2 to 4 carbon atoms and R'' represents a CH₃ or OCH₃ group.

13. A herbicidal preparation as claimed in claim 11 or 12, wherein the carrier is a wetting or dispersing agent, an adhesive, or a liquid or solid carrier, or a grinding agent or a granulating agent.

14. A herbicidal preparation as claimed in claim 11, substantially as described in any one of Examples 29 to 34.

15. A method of treating a crop area, wherein a preparation claimed in any one of claims 11 to 14 is used.

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