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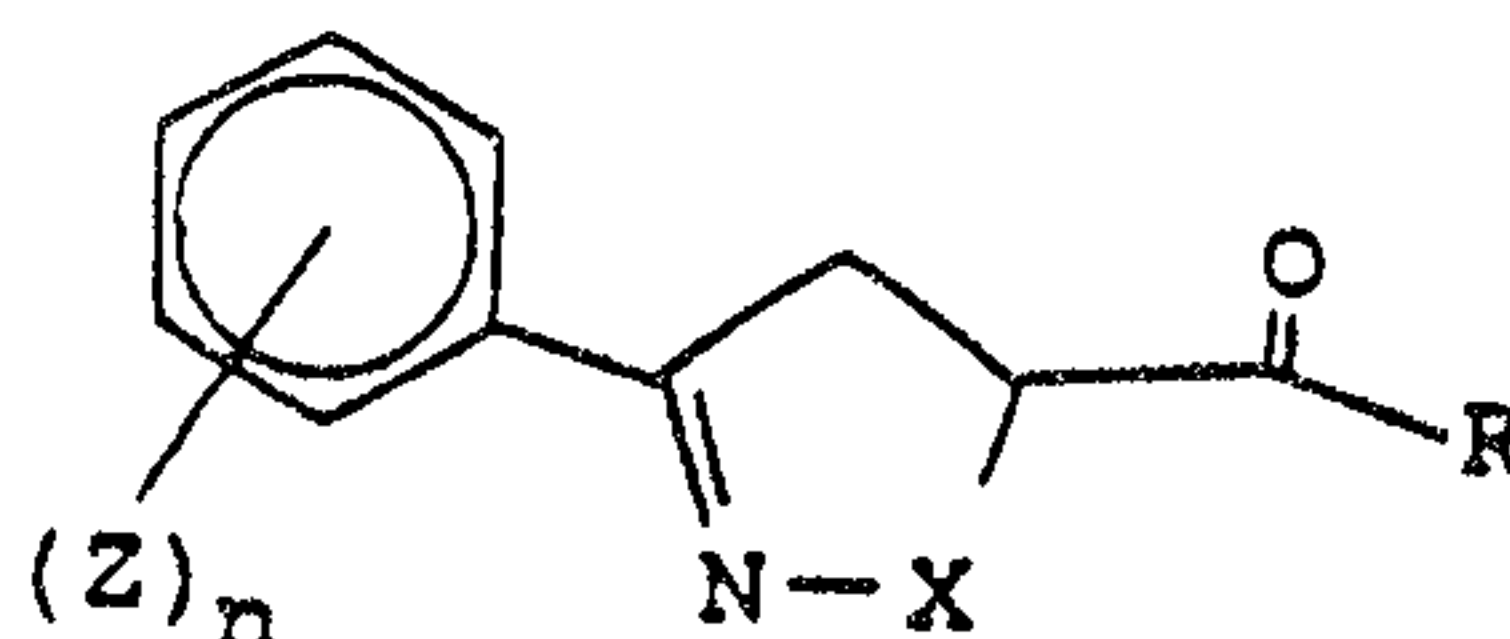
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(54) Titre : AGENTS DE PROTECTION DE VEGETAUX, A BASE D'ISOXAZOLINES OU D'ISOTHIAZOLINES;
NOUVELLES ISOXAZOLINES OU ISOTHIAZOLINES

(54) Title: PLANT-PROTECTING AGENTS CONTAINING ISOXAZOLINES OR ISOTHIAZOLINES, AND NOVEL
ISOXAZOLINES AND ISOTHIAZOLINES



(57) Abrégé/Abstract:

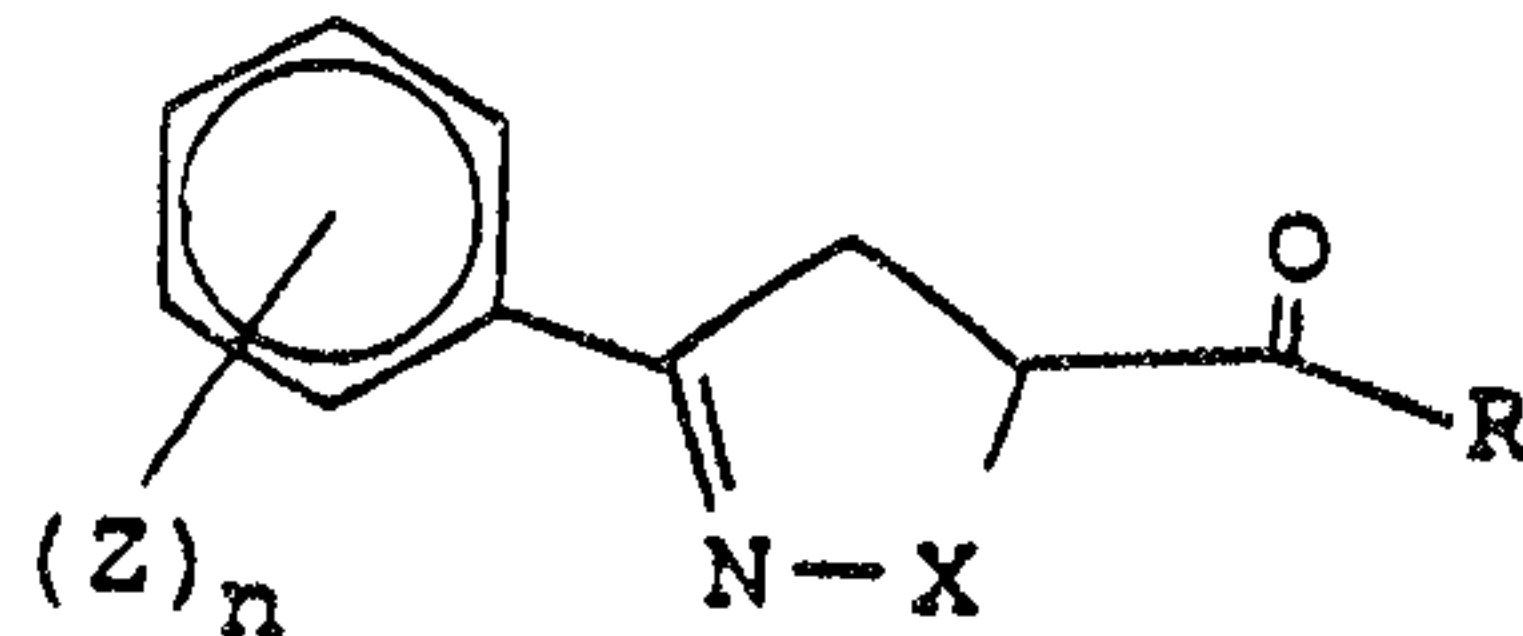
Plant-protecting agents containing isoxazolines or isothiazolines, and novel isoxazolines and isothiazolines Isoxazolines or isothiazolines of the formula (I) or salts thereof (see Formula I) in which (Z)_n, X and R are as defined in claim 1, are suitable as safeners against phytotoxic side effects of herbicides, preferably in cereal crops.



Abstract of the disclosure:

Plant-protecting agents containing isoxazolines or isothiazolines, and novel isoxazolines and isothiazolines

Isoxazolines or isothiazolines of the formula (I) or salts thereof



in which

$(Z)_n$, X and R are as defined in claim 1,

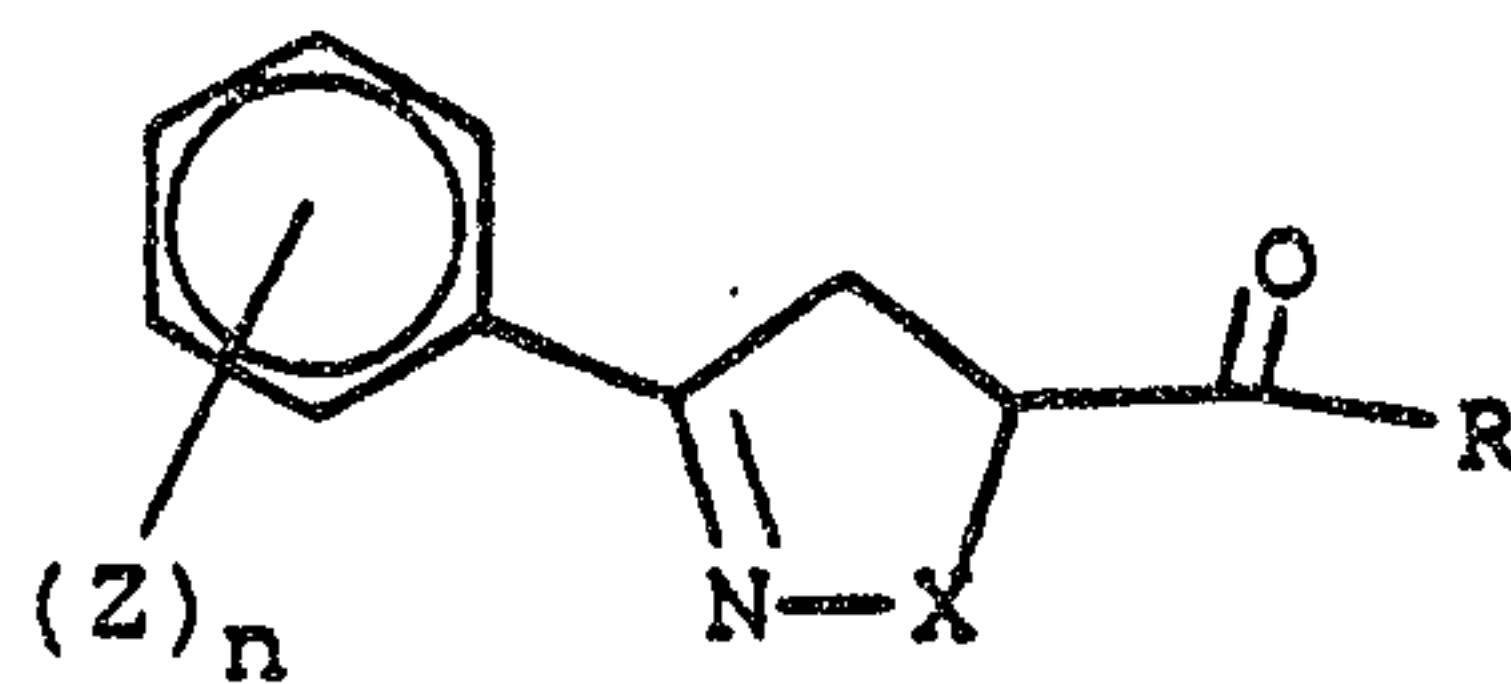
are suitable as safeners against phytotoxic side effects of herbicides, preferably in cereal crops.

Description

Plant-protecting agents containing isoxazoles or isothiazoles, and novel isoxazoles and isothiazoles

5 The invention relates to safeners or antidotes which, in combination with herbicides, can reduce the phytotoxicity of the herbicides to crop plants.

The invention provides plant-protecting agents which contain isoxazoles or isothiazoles of the general formula I or salts thereof,



10 in which

X is an oxygen or sulfur atom, in particular an oxygen atom,

15 R is OH, SH, alkoxy, alkenyloxy, alkynyloxy, alkylthio, alkenylthio, alkynylthio, cycloalkyloxy or cycloalkylthio,

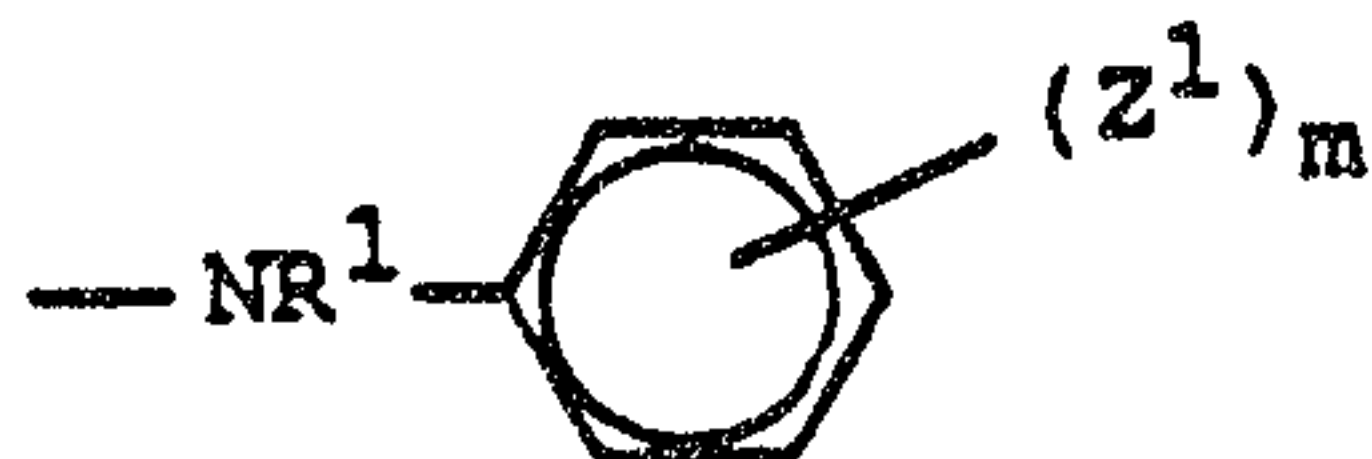
20 where the 8 last-mentioned groups are unsubstituted or mono- or polysubstituted by radicals from the group comprising phenyl, alkoxy, alkenyloxy, alkynyloxy, benzyloxy, phenyloxy, cycloalkyloxy, alkylthio, mono- and dialkylamino, cyano, halogen and NO₂,

25 or is benzyloxy, phenyloxy, benzylthio or phenylthio, where the 4 last-mentioned groups are unsubstituted or mono- or polysubstituted by radicals from the group comprising alkyl, alkenyl, alkynyl, halogen, cyano, NO₂, alkoxy, alkenyloxy, alkynyloxy, alkylthio, mono- and dialkylamino, phenyloxy and benzyloxy,

5

or is trialkylsilylalkoxy, aryldialkylsilyloxy, aralkyldialkylsilyloxy, diarylalkylsilyloxy, diaralkylalkylsilyloxy, a radical of the formula $\text{NR}'\text{R}'$, in which the radicals R' are identical or different radicals from the group comprising alkyl, alkenyl, alkynyl and cycloalkyl, or is pyridino, morpholino, dialkylmorpholino, hydrazino or

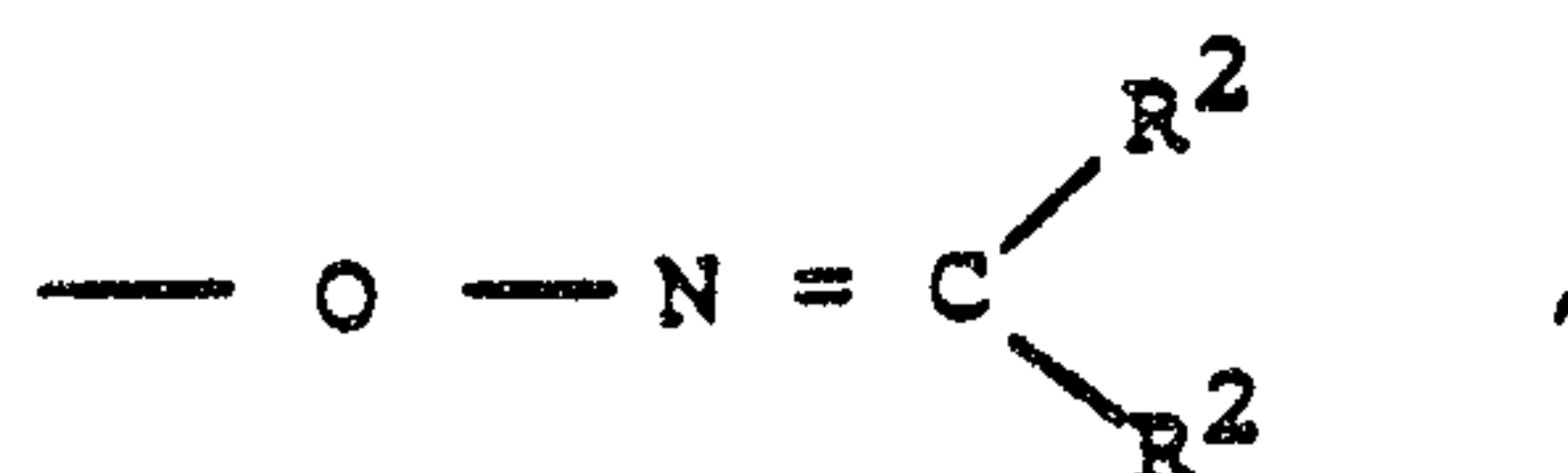
a radical of the formula



10

in which R^1 is a hydrogen atom, alkyl, alkenyl or alkynyl and the radicals Z^1 independently of one another are halogen, nitro, alkyl, alkenyl, alkoxy or phenoxy and m is an integer from 0 to 5, or

is a radical of the formula



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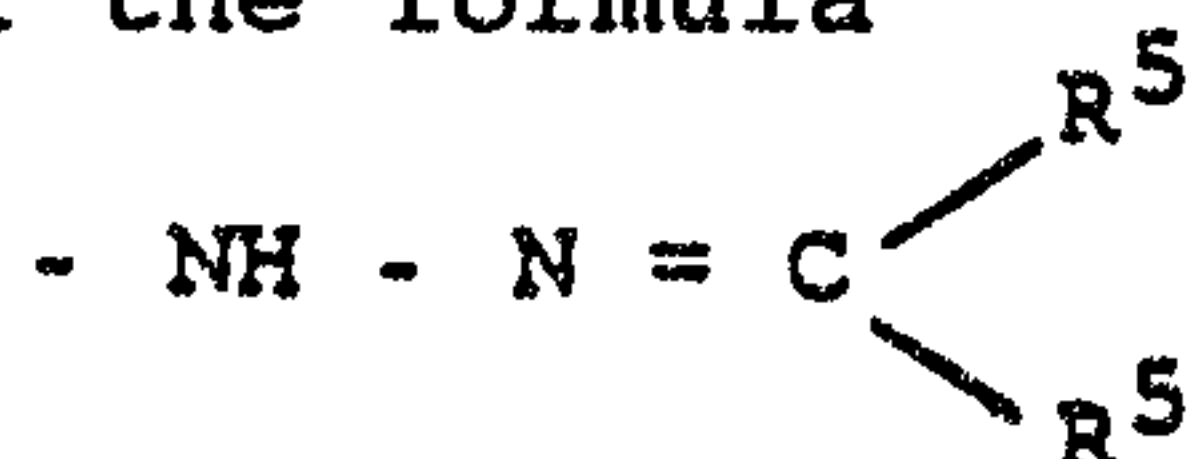
in which the radicals R^2 in each case independently of one another are alkyl, or together with the carbon atom linking them are cycloalkyl, or is



20

in which the R^3 radicals independently of one another are hydrogen, alkyl, alkenyl, alkynyl, aryl, benzyl, alkoxy, alkenyloxy, alkynyloxy or phenoxy and R^4 is hydrogen, alkyl, alkenyl, alkynyl, aryl or benzyl, or

is a radical of the formula



in which the R^5 radicals independently of one another are alkyl, hydrogen or aryl, or together with the carbon atom linking them are cycloalkyl, or

is a radical of the formula



in which the radicals R^6 independently of one another are hydrogen, alkyl, alkenyl, alkynyl, aryl, benzyl, alkoxy, alkenyloxy, alkynyloxy or phenoxy and R^7 has the meaning given above for R ,

10 Z is halogen, nitro, cyano, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, (C_1-C_4) alkylthio, where the alkyl, alkoxy and alkylthio groups independently of one another are unsubstituted or substituted by one or more halogen atoms, in particular fluorine or chlorine, or is
15 (C_3-C_6) cycloalkyl which is unsubstituted or substituted by (C_1-C_4) alkyl, or amino, hydroxymethyl, (C_1-C_4) alkylamino, di (C_1-C_4) alkylamino, (C_1-C_4) alkoxymethyl, where the alkyl and alkoxy groups in the
20 3 last-mentioned radicals independently of one another are unsubstituted or substituted by (C_1-C_4) alkyl, or is phenyl or phenoxy, where phenyl and phenoxy independently of one another are unsubstituted or monosubstituted or polysubstituted by radicals from the group comprising halogen and
25 trifluoromethyl, and

n is an integer from 0 to 5, in particular 0 to 3,

and conventional formulation auxiliaries.

30 The invention furthermore provides selective herbicidal agents which contain an active ingredient of the formula (I) mentioned or salts thereof, in combination with a herbicide and, if desired, customary formulation auxiliaries.

5 In the formula (I), alkyl, alkoxy and alkylthio radicals and the corresponding unsaturated radicals can in each case be straight-chain or branched and preferably have less than 5 carbon atoms. Halogen is fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine, in particular fluorine or chlorine.

10 In the case where $Z = OH$, the compounds of the formula (I) can form salts. Salts which can be employed according to the invention are those which can be used in agriculture. Suitable salts are, for example, metal salts such as alkali metal salts or alkaline earth metal salts, in particular sodium salts or potassium salts, salts with ammonium, mono-, di-, tri- or tetra-(C_1-C_4)alkylammonium or with mono-, di-, tri- or tetra-(C_1-C_4)alkanolammonium.

15 In particular, the invention also provides all stereoisomers and their mixtures which are embraced by the formula (I) but are not specifically defined. Stereoisomers can mainly occur when one or more asymmetric carbon atoms and/or suitably substituted double bonds are present in the compounds of the formula (I). The stereoisomers can be obtained from racemic mixtures by customary separation methods. Alternatively, stereoisomers can be selectively prepared by employing stereoselective reactions using optically active starting substances.

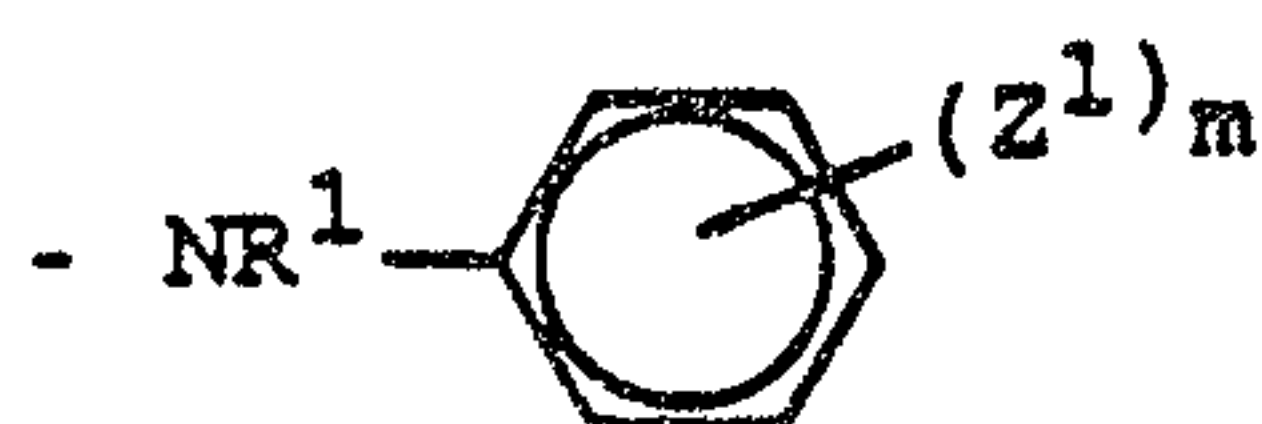
25 Plant-protecting or selective herbicidal agents according to the invention which are of particular interest are those which contain a compound of the formula (I) mentioned in which

30 R is OH , SH , (C_1-C_4)alkoxy, (C_2-C_4)alkenyloxy, (C_2-C_4)alkynyloxy, (C_1-C_4)alkylthio, (C_2-C_4)alkenylthio, (C_2-C_4)alkynylthio, (C_3-C_8)cycloalkoxy or (C_3-C_8)cycloalkylthio, where the 8 last-mentioned groups are unsubstituted or monosubstituted or polysubstituted by radicals from the group comprising
35 phenyl, (C_1-C_4)alkoxy, (C_2-C_4)alkenyloxy, (C_2-C_4)-

alkynyloxy, benzyloxy, phenyloxy, (C₃-C₈)cycloalkyloxy, (C₁-C₄)alkylthio, mono- and di-(C₁-C₄)alkylamino, cyano, halogen and NO₂,

5 or is phenyloxy, phenylthio, benzyloxy or benzylthio, where the 4 last-mentioned groups are unsubstituted or substituted by 1 to 3 radicals from the group comprising (C₁-C₄)alkyl, (C₂-C₄)alkenyl, (C₂-C₄)alkynyl, halogen, cyano, NO₂, (C₁-C₄)alkoxy, (C₂-C₄)alkenyloxy, (C₂-C₄)alkynyloxy, (C₁-C₄)alkylthio,
10 mono- and di-(C₁-C₄)alkylamino, phenyloxy and benzyloxy, or

is a radical of the formula -NR'R' in which R' is (C₁-C₄)alkyl, or is pyridino, morpholino, dimethylmorpholino, hydrazino or a radical of the formula



15 in which R is hydrogen or (C₁-C₄)alkyl, the radicals Z¹ independently of one another are halogen, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy or phenoxy, and m is 0 to 3, or

20 is a radical of the formula -O-N=CR²R² in which the R² radicals are (C₁-C₄)alkyl, in particular methyl, or together with the carbon atom linking them are cyclohexyl or cyclopentyl,

25 or is a radical of the formula -O-CR³R³-CO-R⁴ in which the R³ radicals independently of one another are hydrogen, (C₁-C₄)alkyl, (C₂-C₄)alkenyl, (C₂-C₄)alkynyl, phenyl, benzyl or (C₁-C₄)alkoxy and R⁴ is (C₁-C₄)alkyl, (C₂-C₄)alkenyl, (C₂-C₄)alkynyl, phenyl or benzyl, or

30 is a radical of the formula -NH-N=CR⁵R⁵ in which the R⁵ radicals independently of one another are

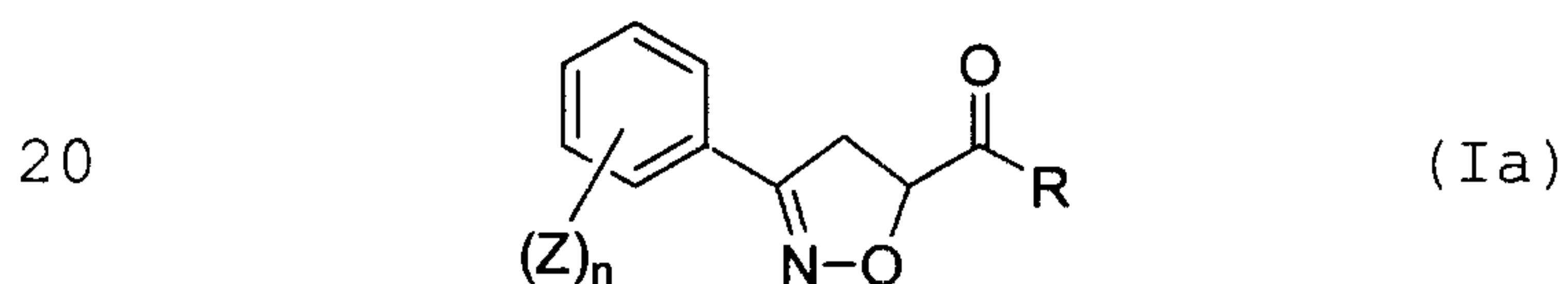
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hydrogen, (C₁-C₄)alkyl or phenyl, or together with the carbon atom linking them are cyclohexyl or cyclopentyl, or is a radical of the formula -O-CR⁶R⁶-CO-R⁷ in which the R⁶ radicals independently of one another are hydrogen, (C₁-C₄)alkyl, (C₂-C₄)alkenyl, (C₂-C₄)alkynyl, phenyl, benzyl or (C₁-C₄)alkoxy and R⁷ has the meaning mentioned for R.

The compounds of Table 1 below represent some of the compounds that are known from the literature, but whose safener action has not been recognized to date; cf., for example, Chem. Ber., Vol. 106, 3275 (1973), Zh. Obs. Khim., Vol. 52 (8), 1932-3 (1982); Chem. Pharm. Bull., Vol. 28 (11), 3296 (1980); Tetrahedron Lett., Vol. 25 (19), 2029 (1984); Aust. J. Chem., Vol. 37 (6), 1217 (1984); Tetrahedron, Vol. 40 (15), 2985 (1984); J. Chem. Soc. Chem. Commun., Vol. 1984 (22), 1523-14 (1984); J. Org. Chem., Vol. 52, 2137 (1987); J. Org. Chem., Vol. 53, 2238 (1988); Chem. Ber., Vol. 106, 3345 (1973) and JP-A-62-103070 (1987):

TABLE 1



(Z) _n	R
H	OCH ₃
3-CH ₃	OCH ₃
25 4-CH ₃	OCH ₃
2,3-Cl ₂	OCH ₃
2,4-Cl ₂	OCH ₃

Table 1 (continuation)

(Z) _n	R
4,5-Cl ₂	-OCH ₃
3-OC ₆ H ₅	-OCH ₃
4-OCF ₂ Br	-OCH ₃
4-OCF ₃	-OCH ₃
2-Cl, 5-NO ₂	-OCH ₃
4-Phenoxyphenyl	-OCH ₃
3-CF ₃	-OCH ₃
3-Cl, 4-F	-OCH ₃
2,6-Cl ₂	-OCH ₃
3-OCF ₂ H	-OCH ₃
3-F	-OCH ₃
4-CF ₃	-OCH ₃
5,6-Cl ₂	-OCH ₃
4,6-Cl ₂	-OCH ₃
3-Br	-OCH ₃
4-CN	-OCH ₃
4-F	-OCH ₃
4-Br	-OCH ₃
3-NO ₂	-OCH ₃
3,4-Cl ₂	-OCH ₃
4-OCHF ₂	-OCH ₃
2-Cl	-OCH ₃
4-NO ₂	-OCH ₃
4-OCH ₃	-OCH ₃
3,4-Cl ₂	OH
4-CF ₃	OH
4-Cl	OH
H	OH
H	-OC ₂ H ₅
4-Cl	-OC ₂ H ₅
4-Cl	-O-isoC ₃ H ₇

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The present invention therefore also provides the compounds of the above-defined formula (I), or salts thereof, which were hitherto unknown. These are compounds of the formula (I) or salts thereof, with the exception of compounds of the
 5 formula (I) in which

X is an oxygen atom, and

a) R is OH or (C₁-C₅)-alkoxy and (Z)_n is an individual radical in the 2-, 3- or 4- position on the phenyl ring from the group comprising F, Cl, Br, CN, OCHF₂, CF₃ and NO₂ or (Z)_n is
 10 3-phenoxy, 2,3-, 2,4-, 2,5-, or 3,4-Cl₂ or 2,4-, 3,4- or 3,5-Br₂ or 3-Cl-4-F, 5-Cl-2-NO₂, or 2-Cl-5-NO₂ or

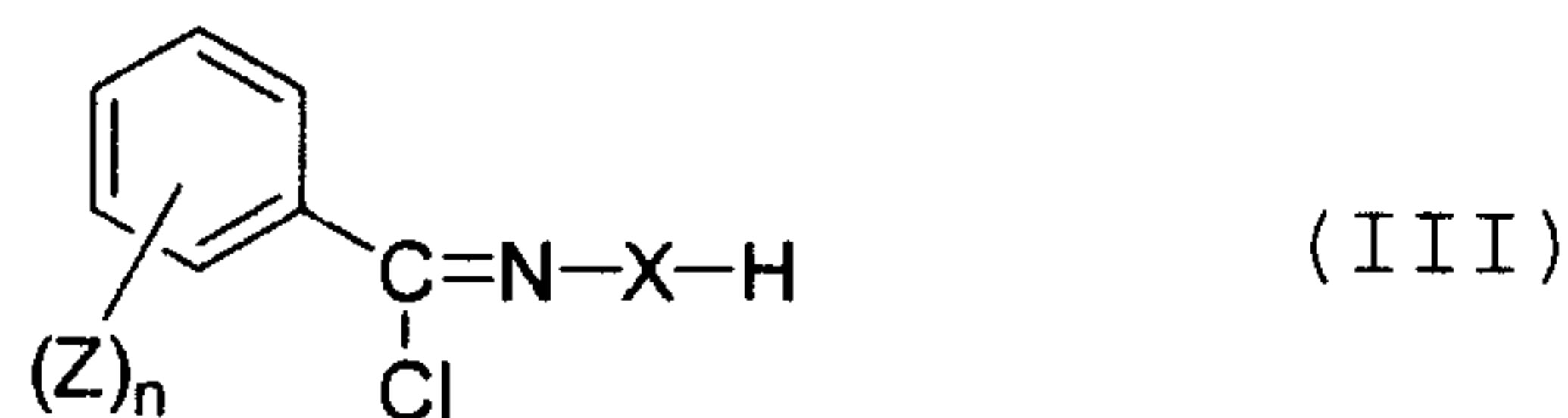
b) R is OCH₃ and (Z)_n is H, 3-CH₃, 4-CH₃, 2,6-, 4,6- or 5,6-Cl₂, 4-OCF₂Br, 4-OCF₃, 4-phenoxy, 4-phenoxyphenyl, 2,4,6-(OCH₃)₃ or 2,4,6-(CH₃)₃ or

15 c) R is OH or OC₂H₅ and (Z)_n is H.

The compounds of the formula (I) which are known and those which were hitherto unknown can be prepared by, or analogously to, the methods described in the literature cited. For example, compounds of the formula (I) are obtained by
 20 reacting an acrylic acid derivative of the formula (II)



with a compound of the formula (III)



25 where R, Z, n and X in the formulae (II) and (III) have the meanings mentioned. The reaction is preferably carried out in

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an aprotic, dipolar organic solvent such as ether at -10°C . up to the boiling point of the solvent and in the presence of an organic base such as

triethylamine or pyridine or an inorganic base such as potassium carbonate, sodium carbonate or sodium bicarbonate.

5 The compounds of the formulae (II) and (III) are known or can be prepared by generally known processes (see, for example, J. Am. Chem. Soc., Vol. 46, 731 (1924); Angew. Chem., Vol. 75, 604 (1963)).

10 The compounds of the formula (I) reduce or prevent phytotoxic side effects of plant protection agents, in particular of herbicides, which can occur when these agents are employed in crops.

15 The compounds of the formula (I) can be applied in succession or together with the herbicidal active ingredients. They are then capable of reducing or completely eliminating harmful side effects of the herbicides in crop plants, without impairing the effectiveness of these herbicides against harmful plants.

20 This makes it possible to considerably enlarge the field of application of conventional herbicides. Compounds which possess the property of protecting crop plants against phytotoxic damage by herbicides are called "antidotes" or "safeners".

25 Examples of herbicides whose phytotoxic side effects can be reduced by means of the compounds of the formula (I) are carbamates, thiocarbamates, haloacetanilides, substituted phenoxy-, naphthoxy- and phenoxyphenoxy-carboxylic acid derivatives as well as heteroaryloxyphenoxy-carboxylic acid derivatives, such as quinolyloxy-, quinoxalyloxy-, pyridyloxy-, benzoxazolyloxy-, benzo-
30 thiazolyloxyphenoxy-carboxylic acid esters, and furthermore dimedone oxime derivatives. Preferred compounds amongst these are phenoxyphenoxy- and heteroaryloxyphenoxyalkane-carboxylic acid esters. Suitable esters in this connection are, in particular, lower alkyl,

alkenyl and alkynyl esters.

The following herbicides may be mentioned by way of example but without imposing any restrictions:

- 5 A) herbicides of the (C₁-C₄)alkyl, (C₂-C₄)alkenyl and (C₃-C₄)alkynyl phenoxyphenoxy- and heteroaryloxyphenoxy-carboxylate type, such as
- 10 methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propionate,
methyl 2-(4-(4-bromo-2-chlorophenoxy)phenoxy)propionate,
methyl 2-(4-(4-trifluoromethylphenoxy)phenoxy)propionate,
10 methyl 2-(4-(2-chloro-4-trifluoromethylphenoxy)phenoxy)-propionate,
methyl 2-(4-(2,4-dichlorobenzyl)phenoxy)propionate,
ethyl 4-(4-(4-trifluoromethylphenoxy)phenoxy)pent-2-enoate,
- 15 ethyl 2-(4-(3,5-dichloropyridyl-2-oxy)phenoxy)propionate,
propargyl 2-(4-(3,5-dichloropyridyl-2-oxy)phenoxy)-propionate,
ethyl 2-(4-(6-chlorobenzoxazol-2-yloxy)phenoxy)-propionate,
- 20 methyl 2-(4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)-phenoxy)propionate,
butyl 2-(4-(5-trifluoromethyl-2-pyridyloxy)phenoxy)-propionate,
methyl 2-(4-(3-fluoro-5-chloropyridyl-2-oxy)phenoxy)-propionate,
- 25 propargyl 2-(4-(3-fluoro-5-chloropyridyl-2-oxy)phenoxy)-propionate,
methyl 2-(4-(6-chloro-2-quinoxalyloxy)phenoxy)propionate,
methyl 2-(4-(6-fluoro-2-quinoxalyloxy)phenoxy)propionate,
30 methyl 2-(4-(6-chloro-2-quinolyloxy)phenoxy)propionate
and
8-methoxycarbonylmethyl 2-(4-(5-chloro-3-fluoropyridin-2-yl)phenoxy)thiopropionate
- B) chloroacetanilide herbicides, such as
- 35 N-(3'-methoxyprop-2'-yl)methyl-6-ethylchloroacetanilide,
N-(3-methyl-1,2,4-oxadiazol-5-ylmethyl)-2',

6'-dimethylchloroacetanilide,

C) thiocarbamates, such as

S-ethyl N,N-dipropylthiocarbamate or

S-ethyl N,N-diisobutylthiocarbamate,

5 D) dimedone derivatives, such as

methyl 3-(1-allyloxyimino)butyl-4-hydroxy-6,6-dimethyl-2-oxocyclohex-3-enecarboxylate

2-(N-ethoxybutyrimidoyl)-5-(2-ethylthiopropyl)-3-hydroxy-2-cyclohexen-1-one,

10 2-(N-ethoxybutyrimidoyl)-5-(2-phenylthiopropyl)-3-hydroxy-2-cyclohexen-1-one,

2-(1-allyloxyiminobutyl)-4-methoxycarbonyl-5,5-dimethyl-3-oxocyclohexenol,

15 2-(1-(3-chloroallyloxy)iminobutyl)-5-(2-ethylthio)-propyl)-3-hydroxycyclohex-2-enone

2-(1-(ethoxyimino)butyl)-3-hydroxy-5-(thian-3-yl)-cyclohex-2-enone or

2-(1-ethoxyiminopropyl)-5-(2,4,6-trimethylphenyl)-3-hydroxy-2-cyclohexen-1-one.

20 The ratio of safener : herbicide can vary within wide limits, in the range between 1 : 10 and 10 : 1, in particular between 2 : 1 and 1 : 10. The amounts of herbicide and safener which are ideal in each case depend on the type of the herbicide used or on the safener used

25 as well as on the nature of the plant stand to be treated, and can be determined in each individual case by appropriate experiments.

The safeners are mainly employed in particular in cereal crops (wheat, rye, barley, oats), rice, maize and sorghum, but also in cotton, sugar beet, sugar cane and soya bean.

30

Depending on their properties, the safeners of the formula (I) can be used for pre-treating the seed of the crop plant (seed dressing), or can be incorporated into

the seed furrows prior to sowing, or used together with the herbicide prior to, or after, plant emergence. Pre-emergence treatment includes both the treatment of the area under cultivation prior to sowing and the treatment of the areas under cultivation where seed has been sown but emergence of the crop plants has not yet taken place. Application together with the herbicide is preferred. Tank mixes or readymixes can be employed for this purpose.

10 Depending on the indication and the herbicide used, the application rates required of the compounds of the formula (I) can vary within wide limits and are generally between 0.01 and 10 kg of active ingredient per hectare.

15 The present invention therefore also relates to a method of protecting crop plants against phytotoxic side effects of herbicides, which comprises applying an effective amount of a compound of the formula (I) before, after, or simultaneously with, the herbicide.

20 Moreover, the compounds according to the invention have growth-regulatory properties in crop plants. They engage in the plant metabolism in a regulating manner and can therefore be employed for simplifying harvesting, for example by triggering desiccation, abscission and stunted growth. Moreover, they are also suitable for generally
25 controlling and inhibiting undesired vegetative growth, without destroying the plants in the process. Inhibition of vegetative growth is highly important in many monocotyledon and dicotyledon crops since lodging can be reduced, or prevented completely, by this method.

30 The compounds of the formula (I) or their combinations with one or more of the herbicides or groups of herbicides mentioned can be formulated in a variety of ways, as predetermined by the biological and/or chemico-physical parameters. The following formulation possibilities are
35 therefore suitable : wettable powders (WP), emulsifiable

concentrates (EC), aqueous solutions (SL), concentrated emulsions such as oil-in-water and water-in-oil emulsions (EW), sprayable solutions or emulsions, oil- or water-based dispersions (SC), dusting agents (DP), seed-dressing agents, soil granules or granules for broadcasting (FG), water-dispersible granules (WG), ULV formulations, microcapsules or waxes.

These individual formulation types are known in principle and are described, for example, in: Winnacker-Küchler, "Chemische Technologie" [Chemical Technology], Volume 7, C. Hauser Verlag, Munich, 4th Ed., 1986; van Valkenburg, "Pesticides Formulations", Marcel Dekker, N.Y., 2nd Ed. 1972-73; K. Martens, "Spray Drying Handbook", 3rd Ed. 1979, G. Goodwin Ltd., London.

The formulation auxiliaries necessary such as inert materials, surfactants, solvents and other additives, are also known and are described, for example, in: Watkins, "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Darland Books, Caldwell, N.J.; H.v.Olphen, "Introduction to Clay Colloid Chemistry", 2nd Ed., J. Wiley & Sons, N.Y.; Marsden, "Solvents Guide", 2nd Ed., Interscience, N.Y. 1950; McCutcheon's "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridgewood N.J.; Sisley and Wood, "Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; Schönfeldt, "Grenzflächenaktive Äthylenoxidaddukte" [Surface-active Ethylene Oxide Adducts], Wiss. Verlagsgesell., Stuttgart, 1976; Winnacker-Küchler, "Chemische Technologie" [Chemical Technology], Volume 7, C. Hauser Verlag, Munich, 4th Ed., 1986.

Combinations with other pesticidally active ingredients, fertilizers and/or growth regulators may also be prepared on the basis of these formulations, for example in the form of a readymix or as a tank mix.

Wettable powders are preparations which are uniformly

dispersible in water and which, besides the active ingredient, also contain wetting agents, for example polyoxyethylated alkylphenols, polyoxyethylated fatty alcohols or fatty amines, alkanesulfonates or alkylarylsulfonates, and dispersants, for example sodium ligninsulfonate, sodium 2,2'-dinaphthylmethane-6,6'-disulfonate, sodium dibutyl-naphthalenesulfonate, or alternatively sodium oleylmethyltaurate, in addition to a diluent or inert substance.

Emulsifiable concentrates are prepared by dissolving the active ingredient in an organic solvent, for example butanol, cyclohexanone, dimethylformamide, xylene and also higher-boiling aromatic compounds or hydrocarbons, with the addition of one or more emulsifiers. Examples of emulsifiers which can be used are: calcium salts of alkylarylsulfonic acids, such as Ca dodecylbenzenesulfonate, or non-ionic emulsifiers, such as fatty acid polyglycol esters, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, propylene oxide/ethylene oxide condensation products (for example block copolymers), alkyl polyglycol ethers, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters or polyoxyethylene sorbitol esters.

Dusting agents can be obtained by grinding the active ingredient with finely divided solid substances, for example talc or natural clays, such as kaolin, bentonite, pyrophyllite or diatomaceous earth.

Soil granules or granules for broadcasting can be produced either by spraying the active ingredient onto adsorptive, granulated inert material or by applying active ingredient concentrates onto the surface of carriers, such as sand, kaolinites or granulated inert material, by means of adhesives, for example polyvinyl alcohol, sodium polyacrylate or, alternatively, mineral oils. Suitable active ingredients can also be granulated in the manner which is conventional for the production of

fertilizer granules, if desired in a mixture with fertilizers.

5 As a rule, the agrochemical preparations contain 0.1 to 99 percent by weight, in particular 0.1 to 95 % by weight, of active ingredient of the formula (I), or of active ingredient mixture with antidote/herbicide, 1 to 99.9 % by weight, in particular 5 to 99.8 % by weight, of a solid or liquid additive, and 0 to 25 % by weight, in particular 0.1 to 25 % by weight, of a surfactant.

10 The concentration of active ingredient in wettable powders is, for example, about 10 to 90 % by weight, the remainder to 100 % by weight being composed of conventional formulation components. In the case of emulsifiable concentrates, the concentration of active
15 ingredients can be about 1 to 80 % by weight, preferably 5 to 80 % by weight. Formulations in the form of dusts usually contain 1 to 25 % by weight, preferably 5 to 20 % by weight, of active ingredient, sprayable solutions about 0.2 to 25 % by weight, preferably 2 to 20 % by
20 weight, of active ingredient. In the case of water-dispersible granules, the active ingredient content depends partly on whether the active compound is liquid or solid. The water-dispersible granules generally contain between 10 and 90 % by weight of active ingre-
25 dient.

In addition, the active ingredient formulations mentioned contain, if appropriate, the adhesives, wetting agents, dispersants, emulsifiers, penetrants, solvents, fillers or carriers which are conventional in each case.

30 For use, the formulations, in commercially available form, are diluted, if appropriate, in a customary manner, for example using water in the case of wettable powders, emulsifiable concentrates, dispersions and water-dispersible granules. Preparations in the form of dusts, soil
35 granules and granules for broadcasting and also sprayable

solutions are usually not further diluted with other inert substances before use.

5 The application rate required for the compounds of the formula (I) varies with the external conditions, such as, inter alia, temperature, humidity, and the nature of the herbicide used. It can vary within wide limits, for example between 0.005 and 10.0 kg/ha or more of active substance, but is preferably between 0.01 and 5 kg/ha.

10 The examples which follow serve to illustrate the invention in greater detail.

A. Formulation Examples

15 a) A dusting agent is obtained by mixing 10 parts by weight of a compound of the formula (I) and 90 parts by weight of talc as inert substance and comminuting the mixture in a hammer mill.

20 b) A wettable powder which is readily dispersible in water is obtained by mixing 25 parts by weight of a compound of the formula (I), 64 parts by weight of kaolin-containing quartz as inert substance, 10 parts by weight of potassium ligninsulfonate and 1 part by weight of sodium oleoylmethyltaurinate as the wetting agent and dispersant, and grinding the mixture in a pinned disk-mill.

25 c) A dispersion concentrate which is readily dispersible in water is obtained by mixing 20 parts by weight of a compound of the formula (I) with 6 parts by weight of alkylphenol polyglycol ether ([®]Triton X 207), 3 parts by weight of isotridecanol polyglycol ether (8 EO) and 71 parts by weight of paraffinic mineral oil (boiling range, for example, about 255 to above 277°C), and grinding the mixture in a ball mill to a
30 fineness of below 5 microns.

d) An emulsifiable concentrate is obtained from 15 parts by weight of a compound of the formula (I), 75 parts by weight of cyclohexanone as solvent and 10 parts by weight of oxyethylated nonylphenol as emulsifier.

5 e) Water-dispersible granules are obtained by mixing

75 parts by weight of a compound of the formula I,

10 " of calcium ligninsulfonate,

5 " of sodium lauryl sulfate,

3 " of polyvinyl alcohol and

10 7 " of kaolin,

grinding the mixture in a pinned disk mill and granulating the powder in a fluidized bed by spraying on water as the granulation liquid.

15 f) Water-dispersible granules are also obtained by homogenizing and precomminuting

25 parts by weight of a compound of the formula (I),

5 " of sodium 2,2'-dinaphthylmethane-6,6'-disulfonate,

2 " of sodium oleoylethyltaurinate,

20 1 part by weight of polyvinyl alcohol,

17 parts by weight of calcium carbonate and

50 " of water,

25 in a colloid mill, subsequently grinding the mixture in a bead mill, and atomizing and drying the resulting suspension in a spray tower by means of a single-fluid nozzle.

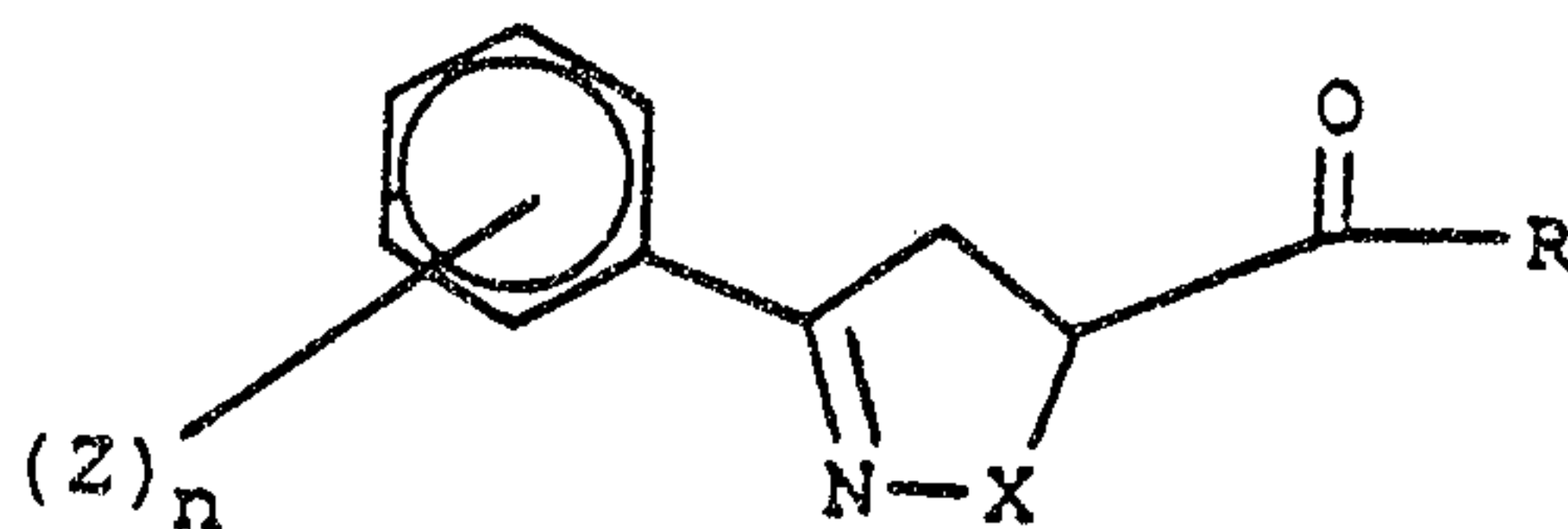
30 g) Analogously to the above formulations, formulations of selective herbicidal agents are obtained when a mixture of an active ingredient of the formula (I) with a herbicide such as, for example, fenoxaprop-ethyl, is employed instead of the active ingredient of the formula (I).

B) Chemical examples:

Ethyl 3-(2-methoxyphenyl)-2-isoxazoline-5-carboxylate
(Example 78, see Table 2)

- 5 50 ml of ethyl acrylate and 4.04 g of triethylamine are introduced into a reaction vessel. 7.4 g of 2-methoxyphenylhydroxamyl chloride in 200 ml of ether are added dropwise to this mixture at 0°C. The mixture is stirred for three hours at room temperature, 50 ml of water are then added and the mixture is extracted with ether.
- 10 The extract is dried over MgSO_4 , and the ether is then distilled off and the crude product is purified on a silica gel column (eluent: n-heptane:ethyl acetate = 8:2). In this manner, 8.4 g (84 % of theory) of the mixed product having a refractive index of $n_D^{20} = 1.544$ are obtained.
- 15 The derivatives in Table 2 which follows are obtained analogously.

Table 2:



Example No.	(Z) _n	R	X	m.p. / n _D ²⁰
1	H	OH	O	197°C
2	"	OCH ₃	"	73°C
3	"	OC ₂ H ₅	"	1.5457
4	"	n-OC ₃ H ₇	"	
5	"	i-OC ₃ H ₇	"	1.5335
6	"	n-OC ₄ H ₉	"	
7	"	O-CH ₂ CO ₂ C ₂ H ₅	"	
8	"	O-C ₆ H ₅	"	
9	"	O-CH ₂ C ₆ H ₅	"	
10	"	OCH ₂ CH=CH ₂	"	
11	"	OCH ₂ C≡CH	"	
12	"	O-CH ₂ Si(CH ₃) ₃	"	
13	"	O ⁻ K ⁺	"	
14	2-Cl	OH	"	
15	"	OCH ₃	"	1.5609
16	"	OC ₂ H ₅	"	1.5519
17	"	n-OC ₃ H ₇	"	
18	"	i-OC ₃ H ₇	"	
19	"	n-OC ₄ H ₉	"	
20	"	O-CH ₂ CO ₂ C ₂ H ₅	"	
21	"	OC ₆ H ₅	"	
22	"	OCH ₂ C ₆ H ₅	"	
23	"	O-CH ₂ CH=CH ₂	"	
24	"	O-CH ₂ C≡CH	"	
25	"	O-CH ₂ Si(CH ₃) ₃	"	
26	"	O ⁻ K ⁺	"	

Table 2, continuation

Example No.	(Z) _n	R	X	m.p. / n _D ²⁰
27	4-Cl	OH	O	
28	"	OCH ₃	"	75°C
29	"	OC ₂ H ₅	"	68°C
30	"	n-OC ₃ H ₇	"	
31	"	i-OC ₃ H ₇	"	
32	"	n-OC ₄ H ₉	"	
33	"	O-CH ₂ CO ₂ C ₂ H ₅	"	
34	"	O-C ₆ H ₅	"	
35	"	O-CH ₂ C ₆ H ₅	"	
36	"	O-CH ₂ CH=CH ₂	"	
37	"	O-CH ₂ C≡CH	"	
38	"	O-CH ₂ Si(CH ₃) ₃	"	
39	2,4-Cl ₂	OH	"	
40	"	OCH ₃	"	58°C
41	"	OC ₂ H ₅	"	64°C
42	"	OC ₃ H ₇ (n)	"	
43	"	OC ₃ H ₇ (iso)	"	
44	"	OC ₄ H ₉ (n)	"	
45	"	O-CH ₂ CO ₂ C ₂ H ₅	"	38°C
46	"	OC ₆ H ₅	"	
47	"	OCH ₂ C ₆ H ₅	"	
48	"	O-CH ₂ CH=CH ₂	"	
49	"	O-CH ₂ C≡CH	"	
50	"	O-CH ₂ Si(CH ₃) ₃	"	
51	"	OCH ₂ CO ₂ CH ₃	"	oil
52	2,6-Cl ₂	OH	"	140°C
53	"	OCH ₃	"	1.5541
54	"	OC ₂ H ₅	"	1.5372
55	"	OC ₃ H ₇ (n)	"	
56	"	OC ₃ H ₇ (iso)	"	
57	"	OC ₄ H ₉ (n)	"	1.5302

Table 2, continuation

Example No.	(Z) _n	R	X	m.p. / n _D ²⁰
58	2,6-Cl ₂	O-CH ₂ CO ₂ C ₂ H ₅	O	
59	"	O-C ₆ H ₅	"	
60	"	O-CH ₂ C ₆ H ₅	"	
61	"	O-CH ₂ CH=CH ₂	"	1.5472
62	"	O-CH ₂ C≡CH	"	67°C
63	"	O-CH ₂ Si(CH ₃) ₃	"	
64	4-OCH ₃	OH	"	
65	"	OCH ₃	"	75°C
66	"	OC ₂ H ₅	"	1.5535
67	"	OC ₃ H ₇ (n)	"	
68	"	OC ₃ H ₇ (iso)	"	
69	"	OC ₄ H ₉ (n)	"	
70	"	O-CH ₂ CO ₂ C ₂ H ₅	"	
71	"	OC ₆ H ₅	"	
72	"	OCH ₂ C ₆ H ₅	"	
73	"	O-CH ₂ CH=CH ₂	"	
74	"	O-CH ₂ C≡CH	"	
75	"	O-CH ₂ Si(CH ₃) ₃	"	
76	2-OCH ₃	OH	"	
77	"	OCH ₃	"	oil
78	"	OC ₂ H ₅	"	1.544
79	"	OC ₃ H ₇ (n)	"	
80	"	OC ₃ H ₇ (iso)	"	
81	"	OC ₄ H ₉ (n)	"	
82	"	O-CH ₂ CO ₂ C ₂ H ₅	"	
83	"	O-C ₆ H ₅	"	
84	"	O-CH ₂ C ₆ H ₅	"	
85	"	O-CH ₂ CH=CH ₂	"	
86	"	O-CH ₂ C≡CH	"	
87	"	O-CH ₂ Si(CH ₃) ₃	"	

Table 2, continuation

Example No.	(Z) _n	R	X	m.p. / n _D ²⁰
88	2-CH ₃	OH	"	
89	"	OCH ₃	"	
90	"	OC ₂ H ₅	"	
91	"	OC ₃ H ₇ (n)	"	
92	"	OC ₃ H ₇ (iso)	"	
93	"	OC ₄ H ₉ (n)	"	
94	"	O-CH ₂ CO ₂ C ₂ H ₅	"	
95	"	OC ₆ H ₅	"	
96	"	OCH ₂ C ₆ H ₅	"	
97	"	O-CH ₂ CH=CH	"	
98	"	O-CH ₂ C≡CH	"	
99	"	O-CH ₂ Si(CH ₃) ₃	"	
100	H	OCH ₃	S	
101	"	OC ₂ H ₅	"	
102	4-Cl	OCH ₃	"	
103	"	OC ₂ H ₅	"	
104	2,4-Cl ₂	OCH ₃	"	
105	"	OC ₂ H ₅	"	
106	2,6-Cl ₂	OCH ₃	"	
107	"	OC ₂ H ₅	"	
108	4-OCH ₃	OCH ₃	"	
109	"	OC ₂ H ₅	"	
110	2-OCH ₃	OCH ₃	"	
111	"	OC ₂ H ₅	"	
112	2-CH ₃	OCH ₃	"	
113	"	OC ₂ H ₅	"	
114	2-Cl	N(CH ₃) ₂	O	
115	"	NHNH ₂	"	
116	"	NH ₂	"	

Table 2, continuation

Example No.	(Z) _n	R	X	m.p./ n _D ²⁰
117	2,4-Cl ₂	N(CH ₃) ₂	O	
118	"	NHNH ₂	"	
119	"	NH ₂	"	
120	4-Cl	N(CH ₃) ₂	"	
121	"	NHNH ₂	"	
122	"	NH ₂	"	

C) Biological examples

5 Example 1

In the greenhouse, wheat and barley were grown in plastic pots until they had reached the 3-4 leaf stage and then treated in succession with compounds according to the invention and herbicides using the post-emergence method. For this purpose, the herbicides and the compounds of the formula (I) were applied in the form of aqueous suspensions or emulsions at a water application rate of 600 to 800 l/ha (converted). 3-4 weeks after the treatment, the plants were scored visually for any type of damage by the herbicides which had been applied, the extent of sustained growth inhibition being particularly taken into account. The plants were assessed in percentages in comparison with untreated controls.

The results from Table 3 demonstrate that the compounds according to the invention are capable of effectively reducing severe herbicide damage on crop plants.

Even when the herbicide H is applied at excessive dosage rates, severe damage which occurs on the crop plants is markedly reduced, and minor damage is prevented completely. Mixtures of herbicides and compounds according to the invention are therefore outstandingly

suitable for selectively controlling weeds in cereal crops.

Table 3

Safener action of the compounds according to the invention

5

Ex. No.	kg of a.i./ha	TRAE	HOVU
H	2.0	80	-
	0.2	-	85
H+40	2.0 + 1.25	20	-
10 H+40	0.2 + 1.25	-	30
H+41	2.0 + 1.25	25	-
H+41	0.2 + 1.25	-	35

Abbreviations:

TRAE = Triticum aestivum

15

HOVU = Hordeum vulgare

a.i. = active ingredient

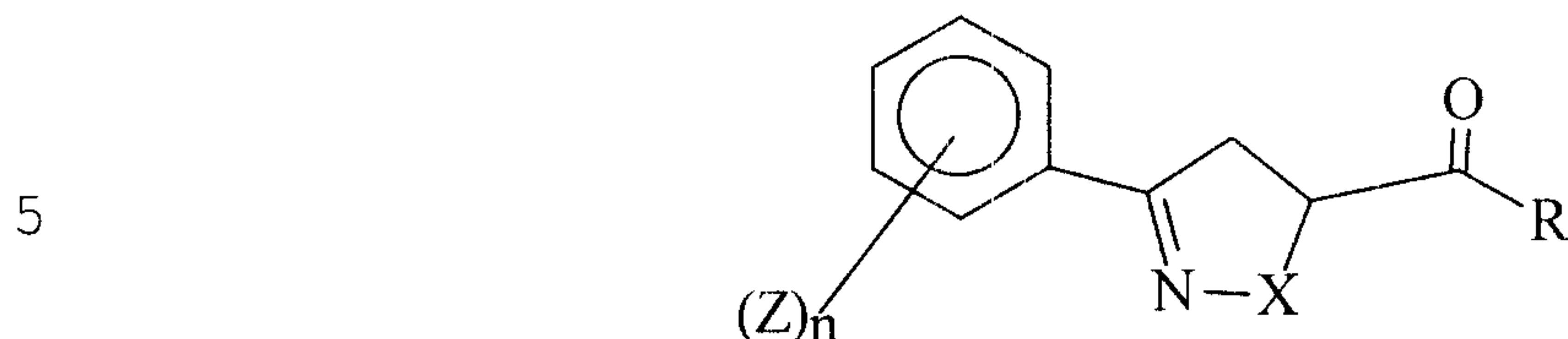
H = ethyl 2-(4-(6-chlorobenzoxazol-2-yloxy)-
phenoxypropionate (fenoxaprop-ethyl)

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CLAIMS:

1. A crop-plant-protecting agent which contains a compound of the formula (I), or a salt thereof,



in which

X is an oxygen or sulfur atom,

R is OH, SH, alkoxy, alkenyloxy, alkynyloxy,
10 alkylthio, alkenylthio, alkynylthio, cycloalkyloxy or
cycloalkylthio,

where the 8 last-mentioned groups are unsubstituted
or mono- or polysubstituted by radicals selected from the group
comprising phenyl, alkoxy, alkenyloxy, alkynyloxy, benzyloxy,
15 phenyloxy, cycloalkyloxy, alkylthio, mono- and dialkylamino,
cyano, halogen and NO₂,

or is benzyloxy, phenyloxy, benzylthio or phenylthio,
where the 4 last-mentioned groups are unsubstituted or mono- or
polysubstituted by radicals selected from the group comprising
20 alkyl, alkenyl, alkynyl, halogen, cyano, NO₂, alkoxy,
alkenyloxy, alkynyloxy, alkylthio, mono- and dialkylamino,
phenyloxy and benzyloxy,

or is trialkylsilylalkoxy, aryldialkylsilyloxy,
aralkyldialkylsilyloxy, diarylalkylsilyloxy,
25 diaralkylalkylsilyloxy, a radical of the formula NR'R', in
which the radicals R' are identical or different radicals
selected from the group comprising alkyl, alkenyl, alkynyl and
cycloalkyl, or is pyridino, morpholino, dialkylmorpholino,

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hydrazino or a radical of the formula $-O-CR^6R^6-CO-R^7$ in which the radicals R^6 independently of one another are hydrogen, alkyl, alkenyl, alkynyl, aryl, benzyl, alkoxy, alkenyloxy, alkynyloxy or phenoxy and R^7 has the meaning given above for R,

5 Z is halogen, nitro, cyano, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, (C_1-C_4) alkylthio, where the alkyl, alkoxy and alkylthio groups independently of one another are unsubstituted or substituted by one or more halogen atoms, or is (C_3-C_6) cycloalkyl which is unsubstituted or substituted by (C_1-C_4) alkyl, or amino, hydroxymethyl, (C_1-C_4) alkylamino, di (C_1-C_4) alkylamino, (C_1-C_4) alkoxymethyl, where the alkyl and alkoxy groups in the 3 last-mentioned radicals independently of one another are unsubstituted or substituted by (C_1-C_4) alkyl, or is phenyl or phenoxy, where phenyl and phenoxy independently of one another are unsubstituted or monosubstituted or polysubstituted by radicals selected from the group comprising halogen and trifluoromethyl, and

n is an integer from 0 to 5,

and one or more herbicides, and optionally
20 conventional formulation auxiliaries.

2. An agent as claimed in claim 1, in which

R is OH, SH, (C_1-C_4) alkoxy, (C_2-C_4) alkenyloxy, (C_2-C_4) alkynyloxy, (C_1-C_4) alkylthio, (C_2-C_4) alkenylthio, (C_2-C_4) alkynylthio, (C_3-C_8) cycloalkoxy or (C_3-C_8) cycloalkylthio,
25 where the 8 last-mentioned groups are unsubstituted or monosubstituted or polysubstituted by radicals selected from the group comprising phenyl, (C_1-C_4) alkoxy, (C_2-C_4) alkenyloxy, (C_2-C_4) alkynyloxy, benzyloxy, phenyloxy, (C_3-C_8) cycloalkyloxy, (C_1-C_4) alkylthio, mono- and di- (C_1-C_4) alkylamino, cyano, halogen
30 and NO_2 ,

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or is a radical of the formula $-O-CR^6R^6-CO-R^7$ in which the R^6 radicals independently of one another are hydrogen, (C_1-C_4) alkyl, (C_2-C_4) alkenyl, (C_2-C_4) alkynyl, phenyl, benzyl or (C_1-C_4) alkoxy and R^7 has the meaning mentioned for R.

5 3. An agent as claimed in claim 1 or 2, which contains, as herbicide, one or more active ingredients selected from the group comprising carbamates, thiocarbamates, haloacetanilides, substituted phenoxy-, naphthoxy-, phenoxyphenoxy-, benzyloxyphenoxy- and heteroaryloxyphenoxyalkanecarboxylic acid
10 derivatives and cyclohexanedione derivatives.

4. An agent as claimed in claim 3, which contains the active ingredient of the formula (I) or a salt thereof and the herbicide in a ratio by weight of from 10 : 1 to 1 : 10.

5. A compound of the formula (I), or a salt thereof, as
15 defined in claim 1 or 2, with the exception of those compounds in which

X is an oxygen atom and

a) R is OH or (C_1-C_5) -alkoxy and $(Z)_n$ is an individual radical in the 2-, 3- or 4- position on the phenyl ring from
20 the group comprising F, Cl, Br, CN, $OCHF_2$, CF_3 and NO_2 or $(Z)_n$ is 3-phenoxy, 2,3-, 2,4-, 2,5-, or 3,4- Cl_2 or 2,4-, 3,4- or 3,5- Br_2 or 3-Cl-4-F, 5-Cl-2- NO_2 , or 2-Cl-5- NO_2 or

b) R is OCH_3 and $(Z)_n$ is H, 3- CH_3 , 4- CH_3 , 2,6-, 4,6- or 5,6- Cl_2 , 4- OCF_2Br , 4- OCF_3 , 4-phenoxy, 4-phenoxyphenyl, 2,4,6-
25 $(OCH_3)_3$ or 2,4,6- $(CH_3)_3$ or

c) R is OH or OC_2H_5 and $(Z)_n$ is H.

6. A plant-protecting agent which contains a compound of the formula (I) or a salt thereof as claimed in claim 5 and customary formulation auxiliaries.

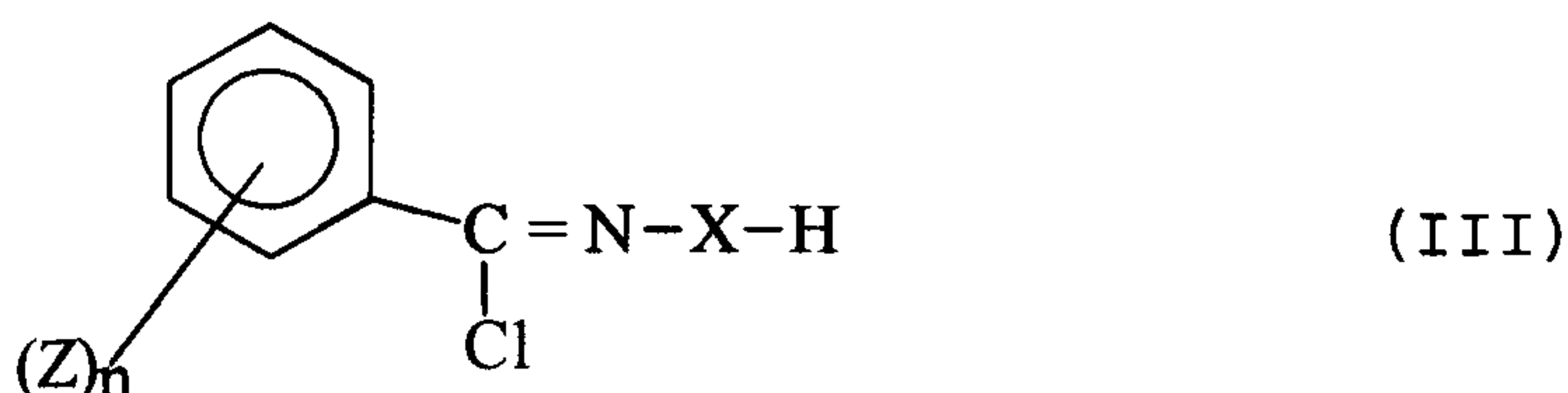
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7. A process for preparing compounds of the formula (I) or salts thereof as claimed in claim 5, which comprises reacting an acrylic acid derivative of the formula (II)



5 with a compound of the formula (III)



where R, Z, n and X in the formulae have the meanings defined
10 in claims 1, 2 and 5.

8. A method of controlling undesired plants in crops of useful plants, which comprises applying a herbicide in combination with compounds of the formula (I), or salts thereof, as defined in claim 1 or 2, to the plants, seeds of
15 plants or the area under cultivation.

9. A method of protecting useful plants against phytotoxic side effects of herbicides, which comprises applying herbicides in combination with compounds of the formula (I), or salts thereof, as defined in claim 1 or 2, to the plants, seeds
20 of plants or the area under cultivation.

10. The use of compounds of the formula (I), or salts thereof, as defined in claim 1 or 2, for protecting plants against phytotoxic side effects of herbicides.

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PATENT AGENTS

