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(54) **HERBICIDAL COMPOSITION**

HERBIZIDE ZUSAMMENSETZUNG

COMPOSITION HERBICIDE

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EP-A- 0 551 650
EP-A- 0 891 709
WO-A-00/00029
WO-A-00/00031
WO-A-00/15615
WO-A-97/34485
US-A- 4 995 902
US-A- 5 741 756

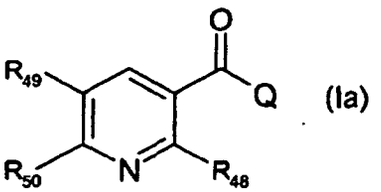
EP 1 250 047 B9

Description

[0001] The present invention relates to a novel herbicidal composition comprising a herbicidal active ingredient combination that is suitable for the selective control of weeds in crops of useful plants, for example in maize crops. The invention relates also to a method of controlling weeds in crops of useful plants, and to the use of the novel composition for that purpose.

[0002] Herbicidally active pyridine ketones are described, for example, in WO 00/15615 and in US-A-4 995 902. Herbicidal synergistic compositions comprising a) a 2-aroyl-(bicyclic 1-one-2-ene-3-ol) compound or a cyclopropyl-isoxazole derivate, b) a second component selected from a set of known herbically active compounds and optionally c) a safener are described in WO 00/00029 and WO 00/00031 respectively. Herbicide/safener combinations containing a) a herbicidally active 2-acylated-1,3-dicarbonyl compound and b) a safener based on N-heterocyclic compounds are described in EP-A-0 551 650.

[0003] The compounds of formula Ia

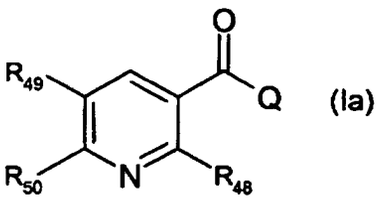


wherein the definitions of the substituents are given hereinbelow have herbicidal activity.

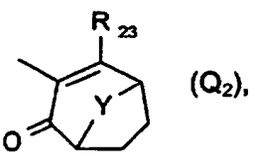
[0004] Surprisingly, it has now been shown that a combination of variable amounts of active ingredients, that is, of an active ingredient of formula Ia with one or more of the active ingredients of formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 listed below, which are known and some of which are also commercially available, exhibits a synergistic action that is capable of controlling, both pre-emergence and post-emergence, the majority of weeds occurring especially in crops of useful plants.

[0005] There is therefore proposed in accordance with the present invention a novel synergistic composition for selective weed control that, in addition to customary inert formulation adjuvants, comprises as active ingredient a mixture of

a) a herbicidally effective amount of a compound of formula Ia



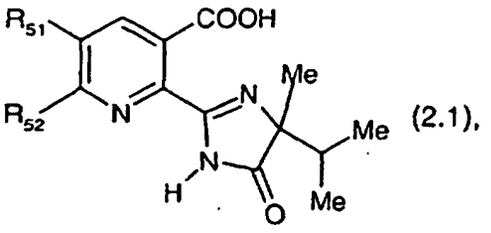
wherein R_{48} is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl or C_1-C_6haloalkyl;
R_{49} is hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, halogen, or phenyl which may be substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;
R_{50} is C_1-C_6haloalkyl; and
Q is the group Q_2



wherein R_{23} is hydroxy and

Y is oxygen, sulfur, a chemical bond or a C_1-C_4alkylene bridge; or an agronomically acceptable salt of such a compound, and

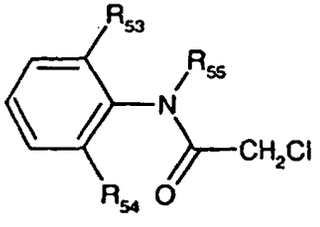
b) a synergistically effective amount of one or more compounds selected from a compound of formula 2.1



(2.1),

wherein R_{51} is CH_2-OMe, ethyl or hydrogen;

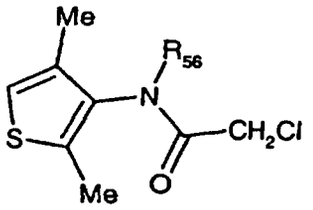
R_{52} is hydrogen or R_{51} and R_{52} together are the group -CH=CH-CH=CH-; and a compound of formula 2.2



(2.2),

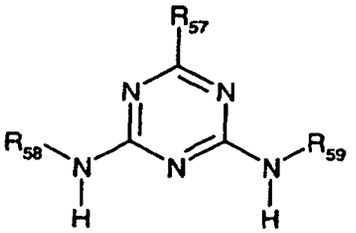
wherein R_{53} is ethyl, R_{54} is methyl or ethyl and R_{55} is -CH(Me)-CH_2OMe <S>-CH(Me)-CH_2OMe, CH_2OMe or CH_2O-CH_2CH_3;

and a compound of formula 2.3



(2.3),

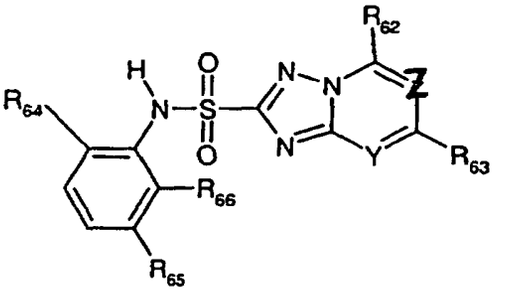
wherein R_{56} is CH(Me)-CH_2OMe or <S>CH(Me)-CH_2OMe; and a compound of formula 2.4



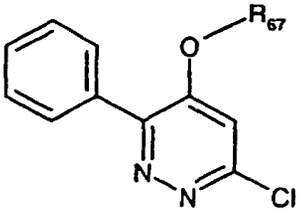
(2.4),

wherein R_{57} is chlorine, methoxy or methylthio, R_{58} is ethyl and R_{59} is ethyl, isopropyl, -C(CN)(CH_3)-CH_3 or tert-butyl;

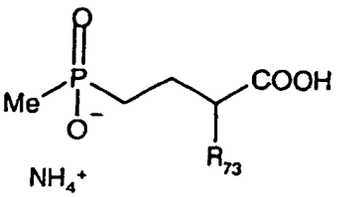
and a compound of formula 2.6


(2.6),

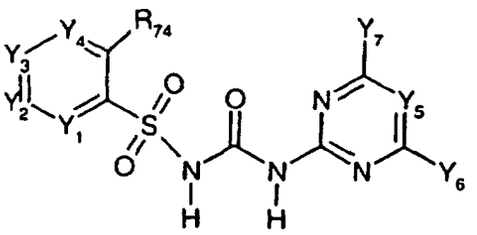
wherein R_{62} is hydrogen, methoxy or ethoxy, R_{63} is hydrogen, methyl, methoxy or fluorine, R_{64} is COOMe, fluorine or chlorine, R_{65} is hydrogen or methyl, Y is methine, C-F or nitrogen, Z is methine or nitrogen and R_{66} is fluorine or chlorine;
and a compound of formula 2.7


(2.7),

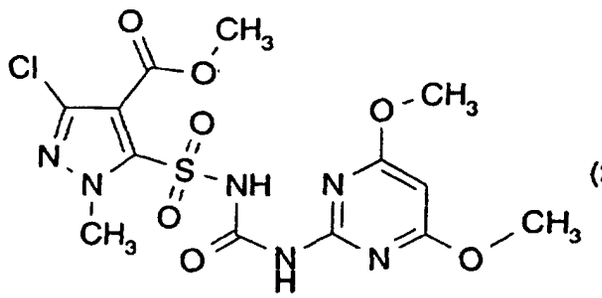
wherein R_{67} is hydrogen or -C(O)-S-n-octyl;
and a compound of formula 2.12


(2.12),

wherein R_{73} is NH_2 or <S>NH_2;
and a compound of formula 2.13

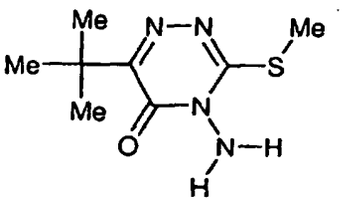

(2.13),

wherein Y_1 is nitrogen, methine, NH-CHO or N-Me, Y_2 is nitrogen, methine or C-I, Y_3 is methine, Y_4 is methine or Y_3 and Y_4 together are sulfur or C-Cl, Y_5 is nitrogen or methine, Y_6 is methyl, difluoromethoxy, trifluoromethyl or methoxy, Y_7 is methoxy or difluoromethoxy and R_{74} is $CONMe_2$, COOMe, $COOC_2H_5$, trifluoromethyl, CH_2-CH_2CF_3 or $SO_2CH_2CH_3$, or a sodium salt thereof ("Me" being in each case the methyl group);
and the compound of formula 2.13.c



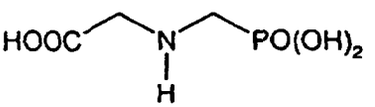
(2.13.c),

and the compound of formula 2.14



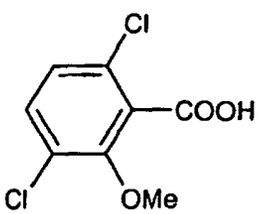
(2.14),

and the compound of formula 2.16



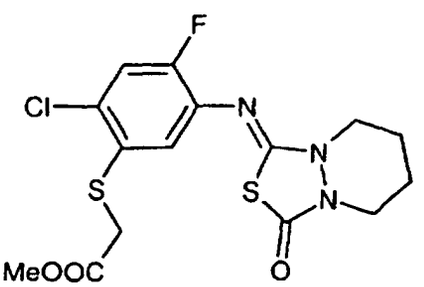
(2.16),

and the compound of formula 2.19



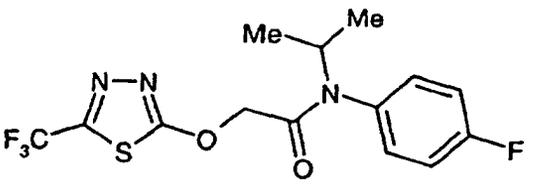
(2.19),

and the compound of formula 2.25



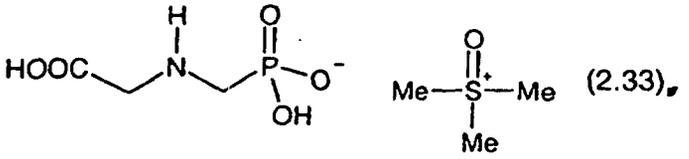
(2.25),

and the compound of formula 2.30



(2.30),

and the compound of formula 2.33



(2.33),

[0006] In the above formulae, "Me" is a methyl group. The alkyl groups appearing in the substituent definitions may be straight-chained or branched and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, or hexyl and also branched isomers thereof. Alkoxy, alkenyl and alkynyl radicals are derived from the mentioned alkyl radicals. The alkenyl and alkynyl groups may be unsaturated once or more than once.
An alkylene group may be substituted by one or more methyl groups; preferably, such alkylene groups are unsubstituted in each case.

[0007] Halogen is, generally, fluorine, chlorine, bromine or iodine. The same correspondingly applies to halogen in the context of other definitions, such as haloalkyl or halophenyl.

[0008] Haloalkyl groups having a chain length of from 1 to 6 carbon atoms are, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1,1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl and 2,2,2-trichloroethyl, pentafluoroethyl, heptafluoro-n-propyl, perfluoro-n-hexyl.

[0009] Suitable haloalkenyl radicals include alkenyl groups substituted one or more times by halogen, halogen being fluorine, chlorine, bromine or iodine and especially fluorine or chlorine, for example 2,2-difluoro-1-methylvinyl, 3-fluoropropenyl, 3-chloropropenyl, 3-bromopropenyl, 2,3,3-trifluoropropenyl, 2,3,3-trichloropropenyl and 4,4,4-trifluorobut-2-en-1-yl. Preferred C_2-C_{12}alkenyl radicals substituted once, twice or three times by halogen are those having a chain length of from 2 to 5 carbon atoms. Suitable haloalkynyl radicals include, for example, alkynyl groups substituted one or more times by halogen, halogen being bromine or iodine and, especially, fluorine or chlorine, for example 3-fluoropropynyl, 3-chloropropynyl, 3-bromopropynyl, 3,3,3-trifluoropropynyl and 4,4,4-trifluoro-but-2-yn-1-yl. Preferred alkynyl groups substituted one or more times by halogen are those having a chain length of from 2 to 5 carbon atoms.

[0010] Alkoxy groups preferably have a chain length of from 1 to 3 carbon atoms. Alkoxy is, for example, methoxy, ethoxy, propoxy, or isopropoxy, preferably methoxy and ethoxy. Haloalkoxy groups preferably have a chain length of from 1 to 3 carbon atoms.

[0011] Haloalkoxy is, for example, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2,2-difluoroethoxy or 2,2,2-trichtoroethoxy, preferably difluoromethoxy, 2-chloroethoxy or trifluoromethoxy.

[0012] The cycloalkyl groups preferably have from 3 to 6 ring carbon atoms and may be substituted by one or more methyl groups; they are preferably unsubstituted, for example cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. Phenyl may be in mono- or poly-substituted form, in which case the substituents may, as desired, be in the ortho-, meta- and/or para-position(s).

[0013] The invention also includes the salts that the compounds of formula Ia may form with amines, alkali metal and alkaline earth metal bases or quaternary ammonium bases. Among the alkali metal and alkaline earth metal hydroxides used as salt formers, emphasis is to be given to the hydroxides of lithium, sodium, potassium, magnesium and calcium, but especially those of sodium and potassium.

[0014] Examples of suitable amines for ammonium salt formation that come into consideration are ammonia as well as primary, secondary and tertiary C_1-C_{18}alkylamines, C_1-C_4hydroxyalkylamines and C_2-C_4alkoxyalkylamines, for example methylamine, ethylamine, n-propylamine, isopropylamine, the four butylamine isomers, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecytamine, hexadecylamine, heptadecylamine, octadecylamine, methyl-ethylamine, methyl-isopropylamine, methylhexylamine, methyl-nonylamine, methyl-pentadecylamine, methyl-octadecylamine, ethylbutylamine, ethyl-heptyiamine, ethyl-octylamine, hexyl-hep-

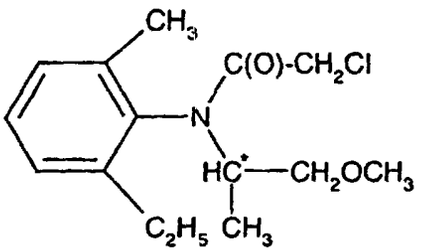
tylamine, hexyl-octylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, isopropanolamine, N,N-diethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, dibutenyl-2-amine, n-hexenyl-2-amine, propylenediamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-sec-butylamine, tri-n-amylamine, methoxyethylamine and ethoxyethylamine; heterocyclic amines, for example pyridine, quinoline, isoquinoline, morpholine, piperidine, pyrrolidine, indoline, quinuclidine and azepine; primary aryl amines for example anilines, methoxyanilines, ethoxyanilines, o-, m- and p-toluidines, phenylenediamines, benzidines, naphthylamines and o-, m- and p-chloroanilines; but especially triethylamine, isopropylamine and diisopropylamine.

[0015] It is extremely surprising that the combination of the active ingredient of formula Ia with one or more active ingredients selected from formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 exceeds the additive effect on the weeds to be controlled that is to be expected in principle, and thus broadens the range of action of the individual active ingredients especially in two respects: Firstly, the rates of application of the individual compounds of formulae Ia and 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 are reduced while a good level of action is maintained and, secondly, the composition according to the invention achieves a high level of weed control also in those cases where the individual substances, in the range of low rates of application, have become unusable from the agronomic standpoint. The result is a considerable broadening of the spectrum of weeds and an additional increase in selectivity in respect of the crops of useful plants, as is necessary and desirable in the event of an unintentional overdose of active ingredient. The composition according to the invention, while retaining excellent control of weeds in crops of useful plants, also enables greater flexibility in succeeding crops.

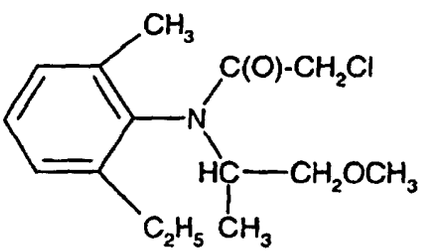
[0016] The composition according to the invention can be used against a large number of agronomically important weeds, such as Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Phaseolus, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum hatepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola and Veronica. The composition according to the invention is suitable for all methods of application conventionally used in agriculture, e.g. pre-emergence application, post-emergence application and seed dressing. The composition according to the invention is suitable especially for controlling weeds in crops of useful plants, such as cereals, rape, sugar beet, sugar cane, plantation crops, rice, maize and soybeans, and also for non-selective weed control.

[0017] "Crops" are to be understood to mean also those crops which have been made tolerant to herbicides or classes of herbicides as a result of conventional methods of breeding or genetic engineering.

[0018] Further preferred synergistic mixtures according to the invention comprise as active ingredients a compound of formula Ia and either a compound of formula 2.2.a



(2.2.a, aRS, 1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloroacetyl-2-ethyl-6-methylaniline), or a compound of formula 2.2.b

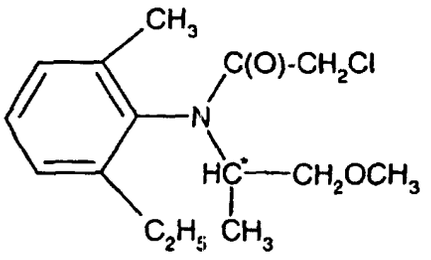


(2.2.b)

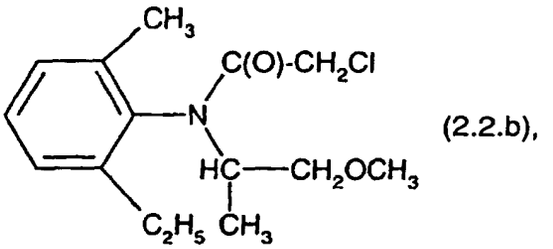
or a compound of formula 2.2 wherein R_{53} is ethyl, R_{54} is methyl and R_{55} is ethoxymethyl, or a compound of formula 2.2 wherein R_{53} is ethyl, R_{54} is ethyl and R_{55} is methoxymethyl, or a compound 2.3, or a compound of formula 2.30,

or a compound of formula 2.4, or a compound of formula 2.13, or a compound of formula 2.14, or a compound of formula 2.6 wherein R_{62} is hydrogen, Z is methine, R_{63} is methyl, Y is nitrogen, R_{64} is fluorine, R_{65} is hydrogen and R_{66} is fluorine, or R_{62} is methoxy, Z is methine, R_{63} is methoxy, Y is methine, R_{64} is chlorine, R_{65} is methyl and R_{66} is chlorine, or a compound of formula 2.7 wherein R_{67} is -C(O)-S-n-octyl, or a compound of formula 2.12, or a compound of formula 2.19, or a compound of formula 2.25, or a compound of formula 2.33, or a compound of formula 2.1.

[0019] Especially preferred synergistic mixtures according to the invention comprise as active ingredients a compound of formula Ia and either a compound of formula 2.2.a



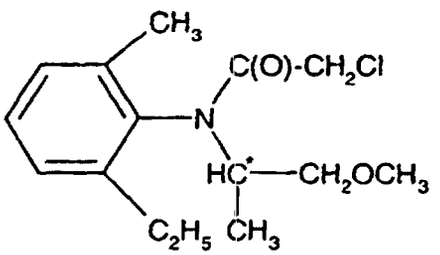
(2.2.a, aRS, 1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloroacetyl-2-ethyl-6-methylaniline), or a compound of formula 2.2.b



(2.2.b),

or a compound of formula 2.2 wherein R_3 is ethyl, R_4 is methyl and R_5 is ethoxymethyl, or a compound of formula 2.2 wherein R_3 is ethyl, R_4 is ethyl and R_5 is methoxymethyl, or a compound of formula 2.3, or a compound of formula 2.30.

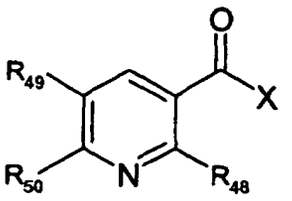
[0020] Combinations of the compounds of formula Ia with the compound of formula 2.2a



(2.2a, aRS,1'S(-)N-(1'-methyi-2'-methoxyethyl)-N-chloroacetyl-2-ethyl-6-methylaniline) have been found to be especially effective, the compound 1.001 indicated hereinbelow under Table 1 being especially preferred as the compound of formula Ia.

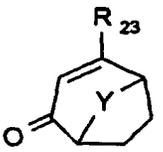
[0021] The compounds of formula Ia can be prepared in a manner analogous to the processes described in WO 97/46530, by

a) reacting a compound of formula II



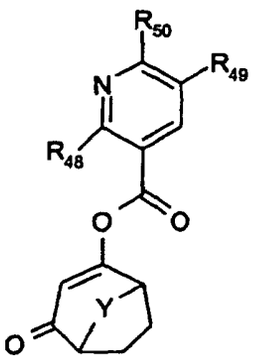
(II),

wherein R_{48}, R_{49} and R_{50} are as defined for formula Ia and X is a leaving group, e.g. halogen, in an inert, organic solvent in the presence of a base, with a compound of formula IV



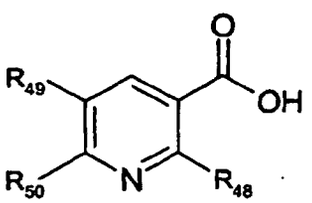
(IV)

wherein R_{23} is hydroxy and Y is as defined for formula Ia, to form a compound of formula VIII



(VIII),

and then isomerising this compound, for example in the presence of a base and a catalytic amount of dimethylaminopyridine (DMAP) or a cyanide source; or
b) reacting a compound of formula XI



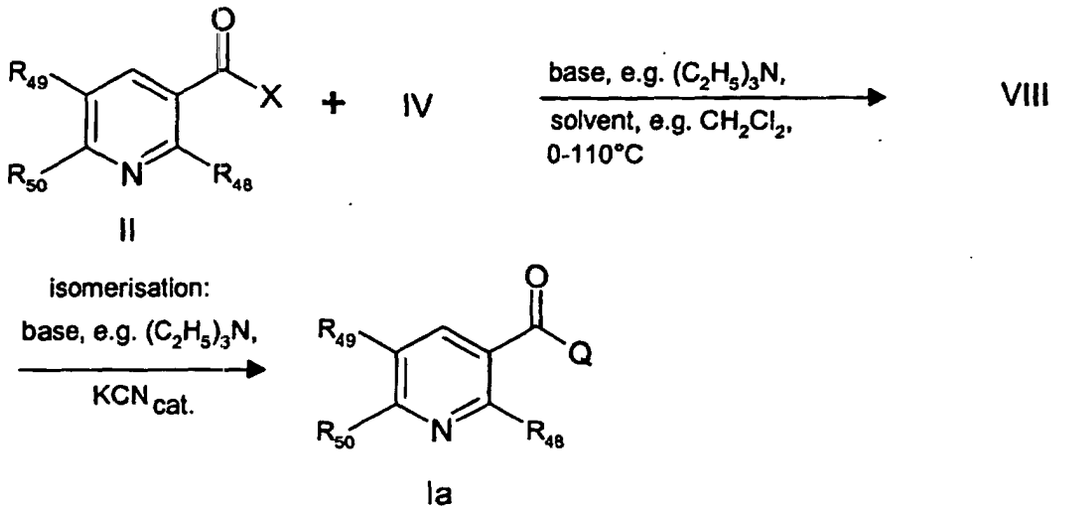
(XI),

wherein R_{48}, R_{49} and R_{50} are as defined for formula Ia, with a compound of formula IV in an inert, organic solvent in the presence of a base and a coupling agent, to form the compound of formula VIII, and then isomerising that compound, for example in the manner described under route a).

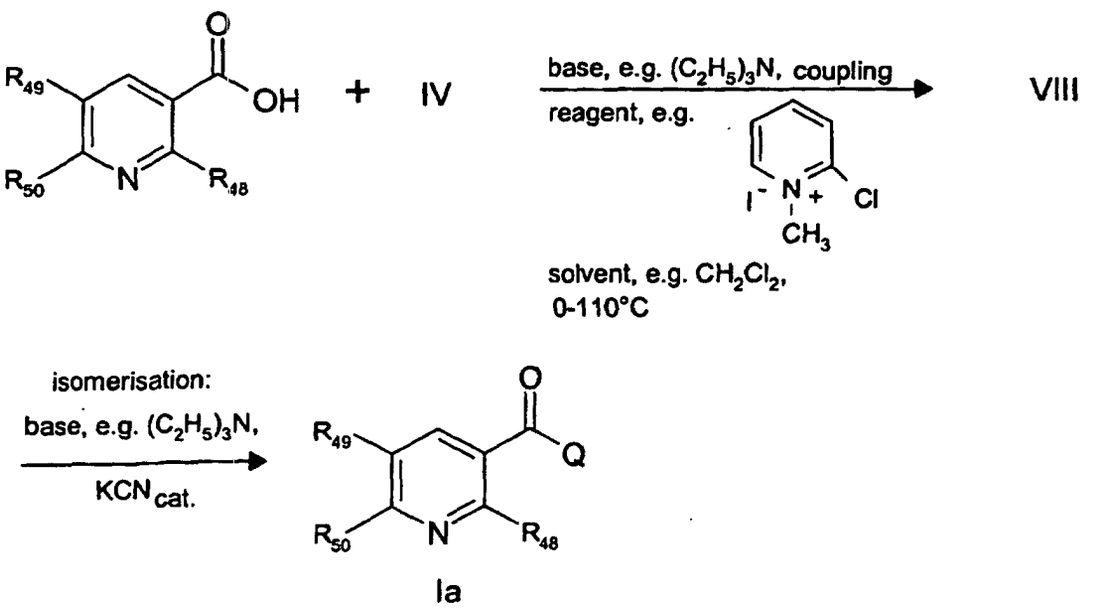
[0022] Preparation of the compounds of formula Ia is illustrated in greater detail in the following Reaction Scheme 1.

Reaction Scheme 1

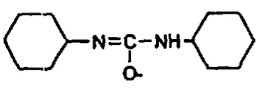
route a):



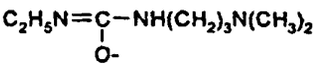
route b):



[0023] For preparation of the compounds of formula Ia there are used as starting materials, in accordance with Reaction Scheme 1, route a), the carboxylic acid derivatives of formula II wherein X is a leaving group, for example halogen, e.g. iodine, bromine or especially chlorine, N-oxyphthalimide or N,O-dimethylhydroxylamino or a moiety of an activated ester, for example



(formed from dicyclohexylcarbodiimide (DCC) and the appropriate carboxylic acid) or



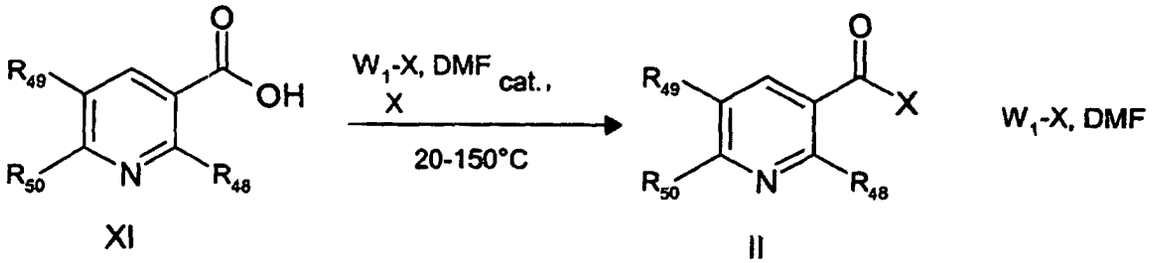
(formed from N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide (EDC) and the appropriate carboxylic acid). Those compounds are reacted in an inert, organic solvent, for example a halogenated hydrocarbon, e.g. dichloromethane, a nitrile, e.g. acetonitrile, or an aromatic hydrocarbon, e.g. toluene, and in the presence of a base, for example an alkylamine, e.g. triethylamine, an aromatic amine, e.g. pyridine or 4-dimethylaminopyridine (DMAP), with the dione derivatives of formula IV to form the isomeric enol ether of formula VIII. The esterification occurs at temperatures of from 0°C to 110°C.

[0024] The isomerisation of the ester derivatives of formulae VIII to form the dione derivatives of formula Ia can be carried out, for example, analogously to EP 369 803 in the presence of a base, for example an alkylamine, e.g. triethylamine, a carbonate, e.g. potassium carbonate, and a catalytic amount of DMAP or a cyanide source, for example acetone cyanohydrin or potassium cyanide.

[0025] According to Reaction Scheme 1, route b), the desired diones of formula Ia can be obtained, for example, analogously to Chem. Lett. 1975, 1045 by means of esterification of the carboxylic acids of formula XI with the dione derivatives of formula IV in an inert solvent, for example a halogenated hydrocarbon, e.g. dichloromethane, a nitrile, e.g. acetonitrile, or an aromatic hydrocarbon, e.g. toluene, in the presence of a base, for example an alkylamine, e.g. triethylamine, and a coupling agent, for example 2-chloro-1-methyl-pyridinium iodide. The esterification occurs, depending on the solvent used, at temperatures of from 0°C to 110°C and yields first, as described under route a), the isomeric ester of formula Ia, which can be isomerised, as described under route a), for example in the presence of a base and a catalytic amount of DMAP, or a cyanide source to form the desired dione derivatives of formula Ia.

[0026] The activated carboxylic acid derivatives of formula II in Reaction Scheme 1 (route a), wherein X is a leaving group, for example halogen, e.g. bromine, iodine or especially chlorine, can be prepared in accordance with known standard procedures, for example as described in C. Ferri "Reaktionen der organischen Synthese", Georg Thieme Verlag, Stuttgart, 1978, page 461 ff and as shown in the following Reaction Scheme 2.

Reaction Scheme 2



[0027] According to Reaction Scheme 2, preparation of the compounds of formula II (X = leaving group) or II (X = halogen) is carried out, for example, by using a halogenating agent, for example a thionyl halide, e.g. thionyi chloride or bromide; a phosphorus halide or phosphorus oxyhalide, e.g. phosphorus pentachloride or phosphorus oxychloride or phosphorus pentabromide or phosphoryl bromide; or an oxalyl halide, e.g. oxalyl chloride, or by using a reagent for the formation of an activated ester for example N,N'-dicyclohexyl-carbodiimide (DCC) or N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide (EDC) of formula X. In the compound of formula X, as a halogenating agent, X, for example, is a leaving group, for example halogen, e.g. fluorine, bromine or iodine and especially chlorine, and W_1 is, for example, PCl_2, SOCI, SOBr or CICOCO.

The procedure is optionally carried out in an inert, organic solvent, for example in an aliphatic, halogenated aliphatic, aromatic or halogenated aromatic hydrocarbon, e.g. n-hexane, benzene, toluene, xylenes, dichloromethane, 1,2-dichloroethane or chlorobenzene, at reaction temperatures in the range from -20°C to the reflux temperature of the reaction mixture, preferably at from 40 to 150°C, and in the presence of a catalytic amount of N,N-dimethylformamide. Such reactions are generally known and described in the literature in a number of variants with respect to the leaving group X.

[0028] The compounds of formulae IV are known and can be prepared in an analogous manner to that described, for example, in EP 338 992.

[0029] The compounds of formulae II and XI are known and can be prepared in an analogous manner to that described, for example, in WO 97/46530, Heterocycles, 48, 779 (1998), Heterocycles, 46, 129 (1997) or Tetrahedron

Letters, 1749 (1998).

[0030] For the preparation of all further compounds of formula Ia functionalised according to the definitions of R_{48}, R_{49} and R_{50}, a large number of known standard procedures, for example alkylation, halogenation, acylation, amidation, oximation, oxidation and reduction, are available, the choice of a suitable preparation procedure being governed by the properties (reactivities) of the substituents in the respective intermediates. Examples of such reactions are given in WO 97/46353.

[0031] All further compounds falling within the scope of formula Ia can be prepared by simple means, taking into account the chemical properties of the pyridyl and Q moieties.

[0032] The end products of formula Ia can be isolated in customary manner by concentration or evaporation of the solvent and can be purified by recrystallisation or trituration of the solid residue in solvents in which they are not readily soluble, such as ethers, aromatic hydrocarbons or chlorinated hydrocarbons, by distillation or by means of column chromatography and a suitable eluant.

[0033] Furthermore, the person skilled in the art will be familiar with the sequence in which certain reactions should advantageously be performed in order to avoid possible subsidiary reactions.

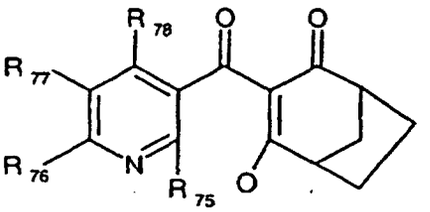
Where synthesis is not directed at the isolation of pure isomers, the product may be in the form of a mixture of two or more isomers. The isomers can be separated according to methods known *per se.*

Preparation Examples:

Example P1: Preparation of 4-hydroxy-3-(2-methyl-6-trifluoromethyl-pyridine-3-carbonyl)-bicyclo[3.2.1]oct-3-en-2-one:

[0034] 6.68 g (0.0305 mol) of 2-methyl-6-trifluoromethyl-nicotinic acid methyl ester (prepared in the manner described in Heterocycles, 46, 129 (1997)) are dissolved in 250 ml of methanol/water (3:1 mixture) and 1.92 g (0.046 mol) of lithium hydroxide hydrate are added in portions at 22°C. After 4 hours at 22°C, the reaction mixture is added to ethyl acetate and 2N hydrochloric acid; the organic phase is washed three times with water, dried with sodium sulfate and concentrated by evaporation, and the residue is triturated with a small amount of hexane. After filtering, 5.69 g (90 % of theory) of the expected 2-methyl-6-trifluoromethyl-nicotinic acid having a melting point of 147-149°C are obtained. The 2-methyl-6-trifluoromethyl-nicotinic acid (2.0 g, 0.0098 mol) obtained is dissolved in 20 ml of oxalyl chloride. Three drops of dimethylformamide are added and the mixture is refluxed for 1 hour. The mixture is then concentrated using a rotary evaporator and the residue (2-methyl-6-trifluoromethyl-nicotinoyl chloride) is taken up in 30 ml of methylene chloride. At 0°C, 2.7 ml (0.0196 mol) of triethylamine and 0.12 g (0.00098 mol) of dimethylaminopyridine are added, and then 1.49 g (0-0 108 mol) of bicyclo[3.2.1]oct-2,4-dione, dissolved in 20 ml of methylene chloride, are added dropwise. After 3 hours at 22°C, the reaction mixture is extracted by shaking with 2N hydrochloric acid. The separated methylene chloride phase is washed with water and then extracted by shaking with 10 % aqueous sodium bicarbonate solution, dried over sodium sulfate and concentrated by evaporation. 3.18 g (100 % of theory) of 2-methyl-6-trifluoromethyl-nicotinic acid 4-oxo-bicyclo[3.2.1]oct-2-en-2-yl ester are obtained in the form of an oil, which can be used further without purification. 3.02 g (0.0093 mol) of methyl-6-trifluoromethyl-nicotinic acid 4-oxo-bicyclo[3.2.1]oct-2-en-2-yl ester and 1.9 ml (0.0136 mol) of triethylamine are dissolved in 45 ml of acetonitrile. At 22°C, 0.01 ml of acetone cyanohydrin is added. After 18 hours at 22°C, the reaction mixture is poured onto a mixture of water and 2N hydrochloric acid and extracted by shaking with ethyl acetate. The ethyl acetate phase is washed with water and then with brine, dried over sodium sulfate and concentrated by evaporation, and the residue is dissolved in a small amount of warm acetone. On being left to stand, the product crystallises out. After filtering, 0.99 g (33 % of theory) of the expected 4-hydroxy-3-(2-methyl-6-trifluoromethyl-pyridine-3-carbonyl)-bicyclo[3.2.1]oct-3-en-2-one is obtained in the form of white crystals (m.p. 75-77°C).

Table 1: Compounds of formula Ib:



(Ib)

Compd. no.	R_{75}	R_{76}	R_{77}	R_{78}	m.p. (°C)
1.001	CH_3	CF_3	H	H	75-77
1.002	CH_3CH_2	CF_3	H	H	
1.003	$(CH_3)_2CH$	CF_3	H	H	111-112
1.004	$CH_3(CH_2)_3$	CF_3	H	H	
1.005	CH_2Br	CF_3	H	H	

Compd. no.	R_{75}	R_{76}	R_{77}	R_{78}	m.p. (°C)
1.006	CH_3	CF_3CF_2	H	H	
1.007	CH_3CH_2	CF_3CF_2	H	H	
1.008	$(CH_3)_2CH$	CF_3CF_2	H	H	
1.009	$CH_3(CH_2)_3$	CF_3CF_2	H	H	
1.010	CH_2Br	CF_3CF_2	H	H	
1.011	CH_3	CHF_2	H	H	
1.012	CH_3CH_2	CHF_2	H	H	
1.013	$(CH_3)_2CH$	CHF_2	H	H	
1.014	$CH_3(CH_2)_3$	CHF_2	H	H	
1.015	CH_2Br	CHF_2	H	H	

Compd. no.	R_{75}	R_{76}	R_{77}	R_{78}	m.p. (°C)
1.016	CH_3	CF_3	CH_3	H	
1.017	CH_3CH_2	CF_3	CH_3	H	
1.018	$(CH_3)_2CH$	CF_3	CH_3	H	
1.019	$CH_3(CH_2)_3$	CF_3	CH_3	H	
1.020	CH_2Br	CF_3	CH_3	H	
1.021	CH_3	CF_3CF_2	CH_3	H	
1.022	CH_3CH_2	CF_3CF_2	CH_3	H	
1.023	$(CH_3)_2CH$	CF_3CF_2	CH_3	H	
1.024	$CH_3(CH_2)_3$	CF_3CF_2	CH_3	H	—
1.025	CH_2Br	CF_3CF_2	CH_3	H	

Compd. no.	R_{75}	R_{76}	R_{77}	R_{78}	m.p. (°C)
1.026	CH_3	CHF_2	CH_3	H	
1.027	CH_3CH_2	CHF_2	CH_3	H	
1.028	$(CH_3)_2CH$	CHF_2	CH_3	H	
1.029	$CH_3(CH_2)_3$	CHF_2	CH_3	H	
1.030	CH_2Br	CHF_2	CH_3	H	

[0035] Compounds of formulae 2.1, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, and 2.13c are known by the names imazamox, imazethapyr, imazaquin, imazapyr, dimethenamid, atrazine, terbuthylazine, simazine, terbutyrn, cyanazine, ametryn, terbumeton, flumetsutam, metosulam, pyridate, glufosinate, primisulfuron, prosulfuron, rimsulfuron, halosulfuron, nicosulfuron, ethoxysulfuron, flazasulfuron and thifensulfuron and are described in the Pesticide Manual, eleventh ed., British Crop Protection Council, 1997 under the entry numbers 412, 415, 414, 413, 240, 34, 692, 651, 693, 168, 20, 691, 339, 495, 626, 382, 589, 613, 644, 389, 519, 287, 325 and 704. The compound of formula 2.13 wherein Y_1, Y_3 and Y_4 are methine, Y_2 is C-I, R_{74} is COOMe, Y_5 is nitrogen, Y_6 is methyl and Y_7 is methoxy is known by the name iodosulfuron (especially the sodium salt) from AGROW No. 296, 16th January 1998, page 22. The compound of formula 2.13 wherein Y_1, Y_2, Y_3 and Y_4 are methine, R_{74} is trifluoromethyl, Y_5 is nitrogen, Y_6 is trifluoromethyl and Y_7 is methoxy is known by the name tritosulfuron and described in DE-A-40 38 430. The compound of formula 2.13 wherein Y_1 is NH-CHO, Y_2, Y_3 and Y_4 are methine, R_{74} is $CONMe_2$, Y_5 is methine and Y_6 and Y_7 are methoxy is described, for example, in WO 95/29899.

The S enantiomer of the compound of formula 2.12 is registered under the CAS-Reg. No. [35597-44-5]. The compound of the general formula 2.2, aRS,1'S(-)N-(1'-methyl-2'-methoxy-ethyl)-N-chloroacetyl-2-ethyl-6-methylaniline, and a compound of the general formula 2.3, (1S,aRS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)-

acetamide, are described, for example, in WO 97/34485. The compound of formula 2.6 wherein R_{62} is ethoxy, R_{63} is fluorine, Y is methine, R_{64} is methoxycarbonyl, R_{65} is hydrogen and R_{66} is chlorine is known by the name cloransulam, for example from AGROW No. 261, 2nd August 1996, page 21. The compound of formula 2.6 wherein R_{62} is methoxy, R_{63} is hydrogen, Y is C-F, R_{64} is fluorine, R_{65} is hydrogen and R_{66} is fluorine, is known by the name florasulam and described in US-A-5 163 995.

[0036] Furthermore, the following compounds of the composition according to the invention are described in the Pesticide Manual, eleventh ed., British Crop Protection Council, 1997:

Compound of formula (name)	Pesticide Manual eleventh ed., Entry No.:
2.14 (metribuzin)	497
2.16 (glyphosate)	383
2.19 (dicamba)	210
2.25 (fluthiacet-methyl)	359
2.30 (fluthiamid)	51
2.33 (sulfosate)	383

[0037] The compound of formula 2.7 wherein R_{67} is hydrogen and its preparation are described in US-A-3 790 571; the compound of formula 2.6 wherein R_{62} is ethoxy, Z is nitrogen, R_{63} is fluorine, R_{64} is chlorine, R_{65} is hydrogen and R_{66} is chlorine is described in US-A-5 498 773.

[0038] It is extremely surprising that the combination of the active ingredient of formula Ia with one or more active ingredients selected from formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 exceeds the additive effect on the weeds to be controlled that is to be expected in principle, and thus broadens the range of action of the individual active ingredients especially in two respects: Firstly, the rates of application of the individual compounds of formulae Ia and 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 are reduced while a good level of action is maintained and, secondly, the composition according to the invention achieves a high level of weed control also in those cases where the individual substances, in the range of low rates of application, have become unusable from the agronomic standpoint. The result is a considerable broadening of the spectrum of weeds and an additional increase in selectivity in respect of the crops of useful plants, as is necessary and desirable in the event of an unintentional overdose of active ingredient. The composition according to the invention, while retaining excellent control of weeds in crops of useful plants, also enables greater flexibility in succeeding crops.

[0039] The composition according to the invention can be used against a large number of agronomically important weeds, such as Stellaria, Nasturtium, Agrostis, Oigitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Phaseolus, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum halepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola and Veronica. The composition according to the invention is suitable for all methods of application conventionally used in agriculture, e.g. pre-emergence application, post-emergence application and seed dressing. The composition according to the invention is suitable especially for controlling weeds in crops of useful plants, such as cereals, rape, sugar beet, sugar cane, plantation crops, rice, maize and soybeans, and also for non-selective weed control.

[0040] "Crops" are to be understood to mean also those crops which have been made tolerant to herbicides or classes of herbicides as a result of conventional methods of breeding or genetic engineering.

[0041] The composition according to the invention comprises the active ingredient of formula Ia and the active ingredients of formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 in any mixing ratio, but usually has an excess of one component over the others. Generally, the mixing ratios (ratios by weight) of the active ingredient of formula Ia and the mixing partners of formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 are from 1:2000 to 2000:1, especially from 200:1 to 1:200.

[0042] The rate of application may vary within wide limits and depends on the nature of the soil, the method of application (pre- or post-emergence; seed dressing; application to the seed furrow; no tillage application etc.), the crop plant, the weed to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. The active ingredient mixture according to the invention can generally be applied at a rate of from 1 to 5000 g of active ingredient mixture/ha.

[0043] The mixtures of the compound of formula Ia with the compounds of formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 may be used in unmodified form, that is to say as obtained in the synthesis. Preferably, however, they are formulated in customary manner, together with the adjuvants conventionally used in formulation technology, such as solvents, solid carriers or surfactants, for example into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules. As with the nature of the compositions, the methods of application, such as spraying, atomising,

dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

[0044] The formulations, i.e. the compositions, preparations or mixtures comprising the compounds (active ingredients) of formulae Ia and 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 and, where appropriate, one or more solid or liquid formulation adjuvants, are prepared in a manner known *per se,* e.g. by intimately mixing and/or grinding the active ingredients with the formulation adjuvants, e.g. solvents or solid carriers. In addition, surface-active compounds (surfactants) may also be used in the preparation of the formulations.

[0045] Examples of solvents and solid carriers are given, for example, in WO 97/34485, page 6.

[0046] Depending on the nature of the compound of formula Ia to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties.

[0047] Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, in WO 97/34485, pages 7 and 8.

[0048] Also suitable in the preparation of the herbicidal compositions according to the invention are the surfactants conventionally used in formulation technology, which are described, *inter alia,* in "McCutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981; Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81.

[0049] The herbicidal formulations usually contain from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of active ingredient mixture comprising a compound of formula Ia and the compounds of formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 from 1 to 99.9 % by weight of a solid or liquid formulation adjuvant, and from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant.

[0050] Whereas commercial products are usually formulated as concentrates, the end user will normally employ dilute formulations. The compositions may also comprise further ingredients, such as stabilisers, e.g. vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders, tackifiers, and also fertilisers or other active ingredients. Preferred formulations have especially the following compositions:

(% = percent by weight)

Emulsifiable concentrates:	
active ingredient mixture	1 to 90 %, preferably 5 to 20 %
surfactant	1 to 30 %, preferably 10 to 20 %
liquid carrier	5 to 94 %, preferably 70 to 85 %

Dusts:	
active ingredient mixture	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier	99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:	
active ingredient mixture	5 to 75 %, preferably 10 to 50 %
water	94 to 24 %, preferably 88 to 30 %
surfactant	1 to 40 %, preferably 2 to 30 %

Wettable powders:	
active ingredient mixture	0.5 to 90 %, preferably 1 to 80 %
surfactant	0.5 to 20 %, preferably 1 to 15 %
solid carrier	5 to 95 %, preferably 15 to 90 %

Granules:	
active ingredient mixture	0.1 to 30 %, preferably 0.1 to 15 %
solid carrier	99.5 to 70 %, preferably 97 to 85 %

[0051] The following Examples illustrate the invention further, but do not limit the invention.

F1. Emulsifiable concentrates	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	25 %	50 %
calcium dodecylbenzenesulfonate	6 %	8%	6 %	8 %
castor oil polyglycol ether (36 mol of ethylene oxide)	4 %	-	4 %	4 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	4 %	-	2 %
cyclohexanone	-	-	10 %	20 %
arom. hydrocarbon mixture C_9-C_{12}	85 %	78%	55 %	16 %

[0052] Emulsions of any desired concentration can be obtained from such concentrates by dilution with water.

F2. Solutions	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	50 %	90%
1-methoxy-3-(3-methoxy-propoxy)-propane	-	20 %	20 %	-
polyethylene glycol MW 400	20 %	10 %	-	-
N-methyl-2-pyrrolidone	-	-	30 %	10 %
arom. hydrocarbon mixture C_9-C_{12}	75 %	60 %	-	-

[0053] The solutions are suitable for use in the form of microdrops.

F3. Wettable powders	a)	b)	c)	d)
active ingredient mixture	5 %	25 %	50 %	80 %
sodium lignosulfonate	4%	-	3 %	-
sodium lauryl sulfate	2 %	3 %	-	4 %
sodium diisobutylnaphthalene-sulfonate	-	6 %	5 %	6 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	1 %	2 %	-
highly dispersed silicic acid	1 %	3 %	5 %	10 %
kaolin	88 %	62%	35 %	-

[0054] The active ingredient is mixed thoroughly with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granules	a)	b)	c)	
active ingredient mixture	0.1 %	5%	15 %	
highly dispersed silicic acid	0.9 %	2 %	2 %	
inorganic carrier (Æ 0.1 - 1 mm)	99.0 %	93 %	83 %	
e.g. $CaCO_3$ or SiO_2				

[0055] The active ingredient is dissolved in methylene chloride and applied to the carrier by spraying, and the solvent is then evaporated off *in vacuo.*

F5. Coated granules	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
polyethylene glycol MW 200	1.0 %	2 %	3 %
highly dispersed silicic acid	0.9 %	1 %	2 %

(continued)

F5. Coated granules	a)	b)	c)
inorganic carrier (Æ 0.1 - 1 mm) e.g. $CaCO_3$ or SiO_2	98.0 %	92 %	80 %

[0056] The finely ground active ingredient is uniformly applied, in a mixer, to the carrier moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

F6. Extruder granules	a)	b)	c)	d)
active ingredient mixture	0.1 %	3 %	5 %	15 %
sodium lignosulfonate	1.5 %	2 %	3 %	4 %
carboxymethylcellulose	1.4%	2 %	2 %	2 %
kaolin	97.0 %	93 %	90 %	79 %

[0057] The active ingredient is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

F7. Dusts	a)	b)	c)
active ingredient mixture	0.1 %	1 %	5 %
talcum	39.9 %	49 %	35 %
kaolin	60.0 %	50 %	60 %

[0058] Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding the mixture in a suitable mill.

F8. Suspension concentrates	a)	b)	c)	d)
active ingredient mixture	3 %	10 %	25 %	50 %
ethylene glycol	5 %	5 %	5 %	5%
nonylphenol polyglycol ether (15 mol of ethylene oxide)	-	1 %	2 %	-
sodium lignosulfonate	3 %	3 %	4 %	5 %
carboxymethylcellulose	1 %	1 %	1 %	1 %
37 % aqueous formaldehyde solution	0.2%	0.2 %	0.2 %	0.2%
silicone oil emulsion	0.8 %	0.8 %	0.8 %	0.8 %
water	87 %	79 %	62 %	38 %

[0059] The finely ground active ingredient is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

[0060] It is often more practical for the compound of formula Ia and the mixing partner or partners of formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 to be formulated separately and to be brought together in the desired mixing ratio in the applicator in the form of a "tank mixture" in water shortly before application.

Biological Examples:

[0061] A synergistic effect exists whenever the action of the active ingredient combination of compounds of formula Ia and 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 is greater than the sum of the actions of the active ingredients applied separately.

[0062] The herbicidal action to be expected We for a given combination of two herbicides can be calculated as follows (see COLBY, S.R., "Calculating synergistic and antagonistic response of herbicide combinations", Weeds 15, pages 20-22,1967):

$$We = X + [Y \cdot (100 - X)/100]$$

wherein:

X= percentage herbicidal action on treatment with the compound of formula Ia at rate of application of p kg per hectare, compared with the untreated control (= 0 %).

Y = percentage herbicidal action on treatment with a compound of formula 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 at a rate of application of q kg per hectare, compared with the untreated control.

We = expected herbicidal action (percentage herbicidal action compared with the untreated control) following treatment with the compounds of formulae Ia and 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 at a rate of application of p + q kg of active ingredient per hectare.

[0063] When the action actually observed is greater than the value to be expected We, there is a synergistic effect.

[0064] The synergistic effect of the combinations of a compound of formula Ia with the compounds of formulae 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.12, 2.13, 2.13c, 2.14, 2.16, 2.19, 2.25, 2.30 and 2.33 is demonstrated in the following Examples.

Experiment description - pre-emergence test:

[0065] Monocotyledonous and dicotyledonous test plants are sown in standard soil in plastics pots. Directly after sowing, the test substances are applied in aqueous suspension by spraying (500 litres of water/ha). The rates of application depend on the optimum doses ascertained under field conditions and greenhouse conditions. The test plants are then grown on in the greenhouse under optimum conditions. The tests are evaluated after 36 days (% action, 100 % = plant has died, 0 % = no phytotoxic action).

Experiment description - post-emergence test:

[0066] The test plants are grown to the 2- to 3-leaf stage in plastics pots under greenhouse conditions. A standard soil is used as cultivation substrate. At the 2- to 3-leaf stage, the herbicide is applied to the test plants on its own and as a mixture. The application is carried out using an aqueous suspension of the test substances in 500 litres of water/ha. The rates of application depend on the optimum doses ascertained under field conditions and greenhouse conditions. The tests are evaluated after 33 days (% action, 100 % = plant has died, 0 % = no phytotoxic action).

Table B1:

Pre-emergence action:				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.2.b [300 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.2.b [300 g/ha]	We according to Colby
Chenopodium	**80**	**0**	**95**	**80**
Solanum	**80**	**40**	**98**	**88**
Cyperus	**0**	**0**	**50**	**0**

Table B2:

Pre-emergence action: Compound no. 2.3.a corresponds to formula 2.3 wherein R_{56} is CH(Me)-CH_2OMe.				
Test plant:	Compd. 1.001 [12.5 g/ha]	Compd. 2.3.a [100 g/ha]	Compd. 1.001 [12.5 g/ha] + compd. 2.3.a [100 g/ha]	We according to Colby
Chenopodium	**80**	**20**	**90**	**84**
Solanum	**75**	**60**	**90**	**90**
Cyperus	**0**	**20**	**60**	**20**

Table B3:

Pre-emergence action: Compound no. 2.2.c corresponds to formula 2.2 wherein R_{53} and A_{54} are ethyl and R_{55} is CH_2OMe.				
Test plant:	Compd. 1.001 [12.5 g/ha]	Compd. 2.2.c [100 g/ha]	Compd. 1.001 [12.5 g/ha] + compd. 2.2.c [100 g/ha]	We according to Colby
Chenopodium	**80**	**20**	**90**	**84**
Solanum	**75**	**50**	**95**	**88**
Cyperus	**0**	**0**	**30**	**0**

Table B4:

Pre-emergence action: Compound no. 2.2.d corresponds to formula 2.2 wherein R_{53} is ethyl, R_{54} is methyl and R_{55} is $CH_2O\text{-}CH_2CH_3$.				
Test plant:	Compd. 1.001 [12.5 g/ha]	Compd. 2.2.d [100 g/ha]	Compd. 1.001 [12.5 g/ha] + compd. 2.2.d [100 g/ha]	We according to Colby
Solanum	**75**	**60**	**95**	**90**

Table B5:

Pre-emergence action:				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.30 [100 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.30 [100 g/ha]	We according to Colby
Cyperus	**10**	**0**	**60**	**10**

[0067] In the following Tables, evaluation is carried out after 31 days:

Table B6:

Pre-emergence action: Compound no. 2.4.a corresponds to the compound of formula 2.4 wherein R_{57} is chlorine, R_{58} is ethyl and R_{59} is isopropyl.				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.4.a [250 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.4.a [250 g/ha]	We according to Colby
Polygonum	**0**	**20**	**80**	**20**

Table B7:

Pre-emergence action: Compound no. 2.4.b corresponds to the compound of formula 2.4 wherein R_{57} is chlorine, R_{58} is ethyl and R_{59} is ethyl.				
Test plant: '	Compd. 1.001 [25 g/ha]	Compd. 2.4.b [125 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.4.b [125 g/ha]	We according to Colby
Polygonum	**0**	**0**	**40**	**0**

Table B8:

Pre-emergence action: Compound no. 2.4.c corresponds to the compound of formula 2.4 wherein R_{57} is chlorine, R_{58} is ethyl and R_{59} is tert-butyl.				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.4.c [250 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.4.c [250 g/ha]	We according to Colby
Ipomoea	**70**	**0**	**90**	**70**
Xanthium	**80**	**0**	**100**	**80**

Table B9:

Pre-emergence action: Compound no. 2.4.d corresponds to the compound of formula 2.4 wherein R_{57} is methylthio, R_{58} is ethyl and R_{59} is tert-butyl.				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.4.d [250 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.4.d [250 g/ha]	We according to Colby
Ipomoea	**70**	**0**	**80**	**70**
Xanthium	**80**	**10**	**95**	**82**

Table B10:

Pre-emergence action:				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.14 [125 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.14 [125 g/ha]	We according to Colby
Ipomoea	**70**	**0**	**85**	**70**
Xanthium	**80**	**20**	**100**	**84**

Table B11:

Pre-emergence action: Compound no. 2.6.a corresponds to the compound of formula 2.6 wherein R_{62} is hydrogen, R_{63} is methyl, R_{64} is fluorine, R_{65} is hydrogen, Y is nitrogen, Z is methine and R_{66} is fluorine.				
Test plant:	Compd. 1.001 [50 g/ha]	Compd. 2.6.a [30 g/ha]	Compd. 1.001 [50 g/ha] + compd. 2.6.a [30 g/ha]	We according to Colby
Polygonum	**0**	**30**	**90**	**30**

In the following Tables, evaluation is carried out after 21 days:

Table B12:

Post-emergence action: Compound no. 2.7.a corresponds to the compound of formula 2.7 wherein R_{67} is -C(O)-S-n-octyl.				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.7.a [250 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.7.a [250 g/ha]	We according to Colby
Ipomoea	**30**	**10**	**80**	**30**
Polygonum	**75**	**0**	**95**	**75**
Xanthium	**90**	**10**	**100**	**91**

Table B13:

Post-emergence action:				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.19 [250 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.19 [250 g/ha]	We according to Colby
Ipomoea	**30**	**60**	**95**	**72**

Table B14:

Post-emergence action:				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.16 [360 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.16 [360 g/ha]	We according to Colby
Ipomoea	**30**	**20**	**70**	**46**
Polygonum	**75**	**10**	**90**	**84**

Table B15:

Post-emergence action:				
Test plant:	Compd. 1.001 [12.5 g/ha]	Compd. 2.33 [360 g/ha]	Compd. 1.001 [12.5 g/ha] + compd. 2.33 [360 g/ha]	We according to Colby
Polygonum	**30**	**0**	**90**	**30**

Table B16:

Post-emergence action: Compound no. 2.12.a corresponds to the compound of formula 2.12 wherein R_{73} is NH_2.				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.12.a [400 g/ha]	Compd. 1 .001 [25 g/ha] + compd. 2.12a [400 g/ha]	We according to Colby
Ipomoea	**30**	**20**	**90**	**44**

Table B17:

Post-emergence action:				
Test plant:	Compd. 1.001 [12.5 g/ha]	Compd. 2.25 [2 g/ha]	Compd. 1.001 [12.5 g/ha] + compd. 2.25 [2 g/ha]	We according to Colby
Ipomoea	**30**	**0**	**50**	**30**
Polygonum	**30**	**0**	**40**	**30**

Table B18:

Post-emergence action: Compound no. 2.1.a corresponds to the compound of formula 2.1 wherein R_{52} is hydrogen and R_{51} is ethyl.				
Test plant:	Compd. 1.001 [12.5 g/ha]	Compd. 2.1.a [30 g/ha]	Compd. 1.001 [12.5 g/ha] + compd. 2.1.a [30 g/ha]	We according to Colby
Polygonum	**30**	**30**	**70**	**51**

Table B19:

Post-emergence action: Compound no. 2.1.b corresponds to the compound of formula 2.1 wherein R_{51} is CH_2OMe and R_{52} is hydrogen.				
Test plant:	Compd. 1.001 [25 g/ha]	Compd. 2.1.b [30 g/ha]	Compd. 1.001 [25 g/ha] + compd. 2.1.b [30 g/ha]	We according to Colby
Polygonum	**75**	**30**	**90**	**83**

[0068] In the following Tables, evaluation is carried out after 23 days:

Table B20:

Pre-emergence action: Compound no. 2.13.b corresponds to formula 2.13 wherein R_{74} is -COOMe, Y_1, Y_2, Y_3 and Y_4 are each methine, Y_5 is methine and Y_6 and Y_7 are difluoromethoxy.				
Test plant:	Compd. 1.001 [6 g/ha]	Compd. 2.13.b [15 g/ha]	Compd. 1.001 [6 g/ha] + compd. 2.13.b [15 g/ha]	We according to Colby
Chenopodium	**50**	**70**	**95**	**85**

Table B21:

Pre-emergence action:				
Test plant:	Compd. 1.001 [6 g/ha]	Compd. 2.13.c [60 g/ha]	Compd. 1.001 [6 g/ha] + compd. 2.13.c [60 g/ha]	We according to Colby
Chenopodium	**50**	**10**	**85**	**55**

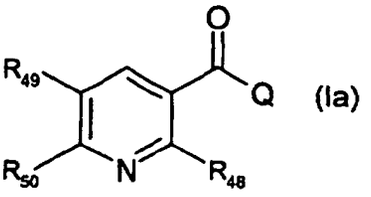
Table B22:

Pre-emergence action: Compound no. 2.13.d corresponds to the compound of formula 2.13 wherein Y_1, Y_2, Y_3 and Y_4 are methine, R_{74} is trifluoromethyl, Y_5 is nitrogen, Y_6 is trifluoromethyl and Y_7 is methoxy.				
Test plant:	Compd. 1.001 [6 g/ha]	Compd. 2.13d [7.5 g/ha]	Compd. 1.001 [6 g/ha] + compd. 2.13.d [7.5 g/ha]	We according to Colby
Amaranthus	**10**	**80**	**95**	**82**

Claims

1. A herbicidally selective composition that, in addition to comprising customary inert formulation adjuvants, comprises as active ingredient a mixture of

a) a herbicidally effective amount of a compound of formula Ia



(Ia)

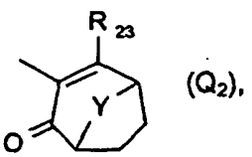
wherein

R_{48} is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl or C_1-C_6haloalkyl;

R_{49} is hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, halogen, or phenyl which may be substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;

R_{50} is C_1-C_6haloalkyl; and

Q is the group Q_2

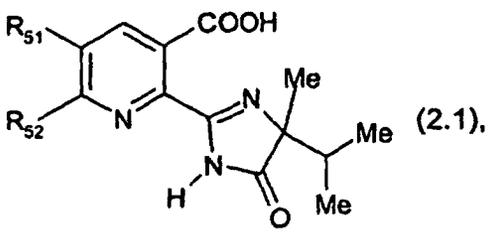


(Q_2),

wherein R_{23} is hydroxy and

Y is oxygen, sulfur, a chemical bond or a C_1-C_4alkylene bridge; or an agronomically acceptable salt of such a compound, and

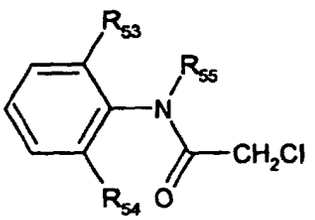
b) a synergistically effective amount of one or more compounds selected from a compound of formula 2:1



(2.1),

wherein R_{51} is CH_2-OMe, ethyl or hydrogen;

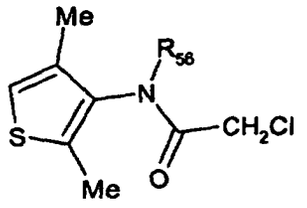
R_{52} is hydrogen or R_{51} and R_{52} together are the group -CH=CH-CH=CH-; and a compound of formula 2.2



(2.2),

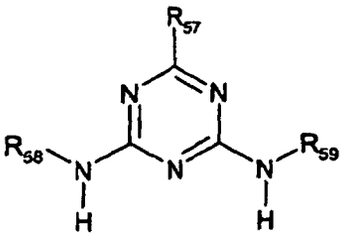
wherein R_{53} is ethyl, R_{54} is methyl or ethyl and R_{55} is -CH(Me)-CH_2OMe, <S>-CH(Me)-CH_2OMe, CH_2OMe or CH_2O-CH_2CH_3;

and a compound of formula 2.3



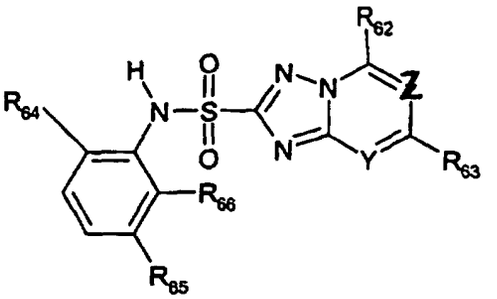
(2.3),

wherein R_{56} is CH(Me)-CH_2OMe or <S>CH(Me)-CH_2OMe; a compound of formula 2.4



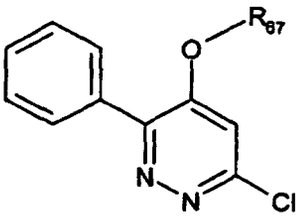
(2.4),

wherein R_{57} is chlorine, methoxy or methylthio, R_{58} is ethyl and R_{59} is ethyl, isopropyl, -C(CN)(CH_3)-CH_3 or tert-butyl; and a compound of formula 2.6



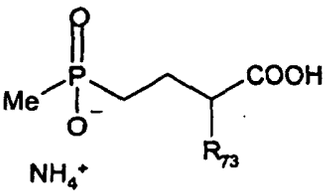
(2.6),

wherein R_{62} is hydrogen, methoxy or ethoxy, R_{63} is hydrogen, methyl, methoxy or fluorine, R_{64} is COOMe, fluorine or chlorine, R_{65} is hydrogen or methyl, Y is methine, C-F or nitrogen, Z is methine or nitrogen and P_{66} is fluorine or chlorine; and a compound of formula 2.7

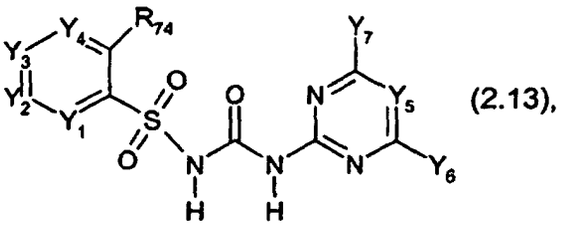


(2.7),

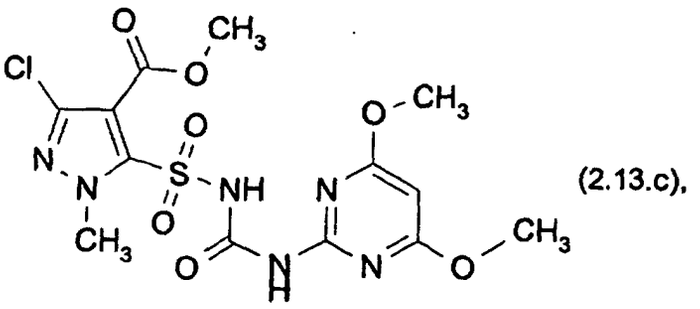
wherein R_{67} is hydrogen or -C(O)-S-n-octyl; and a compound of formula 2.12


(2.12),

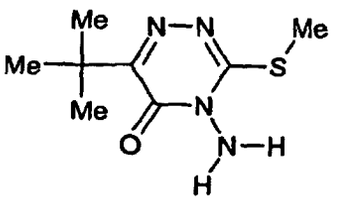
wherein R_{73} is NH_2 or <S>NH_2; a compound of formula 2.13


(2.13),

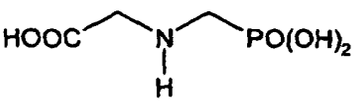
wherein Y_1 is nitrogen, methine, NH-CHO or N-Me, Y_2 is nitrogen, methine or C-I, Y_3 is methine, Y_4 is methine or Y_3 and Y_4 together are sulfur or C-Cl, Y_5 is nitrogen or methine, Y_6 is methyl, difluoromethoxy, trifluoromethyl or methoxy, Y_7 is methoxy or difluoromethoxy and R_{74} is $CONMe_2$, COOMe, $COOC_2H_5$, trifluoromethyl, CH_2-CH_2CF_3 or $SO_2CH_2CH_3$, or a sodium salt thereof; and the compound of formula 2.13.c


(2.13.c),

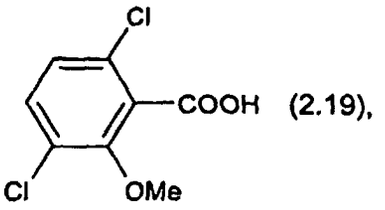
and the compound of formula 2.14


(2.14),

and the compound of formula 2.16

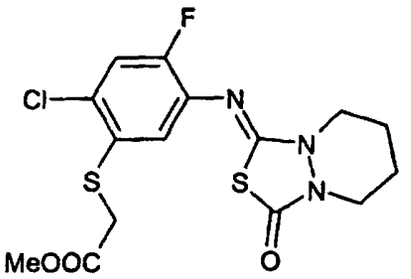

(2.16),

and the compound of formula 2.19



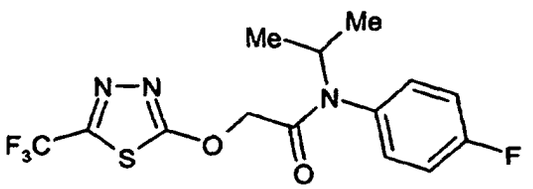
(2.19),

and the compound of formula 2.25



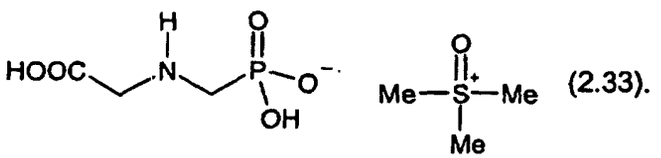
(2.25),

and the compound of formula 2.30



(2.30)

and the compound of formula 2.33



(2.33).

2. A method of controlling undesired plant growth in crops of useful plants, which comprises allowing a herbicidally effective amount of a composition according to claim 1 to act on the crop plant or the locus thereof.

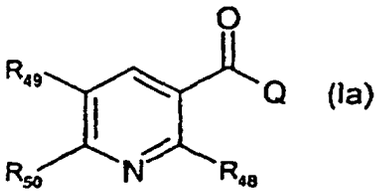
3. A method according to claim 2, wherein the crop plant is maize or sugar cane.

4. A method according to claim 2, wherein the crops of useful plants are treated with the mentioned composition at rates of application corresponding to a total amount of active ingredient of from 1 to 5000 g per hectare.

Patentansprüche

1. Herbizide selektive Zusammensetzung, die zusätzlich zu den üblichen inerten Formulierungszusatzstoffen, als Wirkstoff ein Gemisch aus

a) einer herbizid wirksamen Menge einer Verbindung der Formel Ia



(Ia)

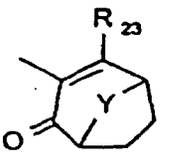
worin

R_{48} C_1-C_6-Alkyl, C_2-C_6-Alkenyl, C_2-C_6-Halogenalkenyl, C_2-C_6-Alkinyl, C_2-C_6-Halogenalkinyl, C_3-C_6-Cycloalkyl oder C_1-C_6-Halogenalkyl ist;

R_{49} Wasserstoff, C_1-C_6-Alkyl, C_1-C_6-Halogenalkyl, Halogen oder Phenyl ist, das durch C_1-C_3-Alkyl, C_1-C_3-Halogenalkyl, C_1-C_3-Alkoxy, C_1-C_3-Halogenalkoxy, Halogen, Cyano oder durch Nitro substituiert sein kann;

R_{50} C_1-C_6-Halogenalkyl ist; und

Q die Gruppe Q_2 ist



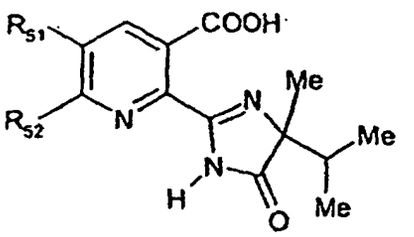
(Q_2),

worin

R_{23} Hydroxy ist; und

Y Sauerstoff, Schwefel, eine chemische Bindung oder eine C_1-C_4-Alkylenbrücke ist; oder einem agronomisch akzeptablen Salz einer solchen Verbindung, und

b) einer synergistisch wirksamen Menge von einer oder mehreren Verbindungen, ausgewählt aus einer Verbindung der Formel 2.1

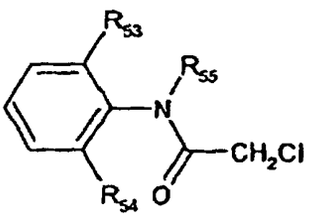


(2.1),

worin

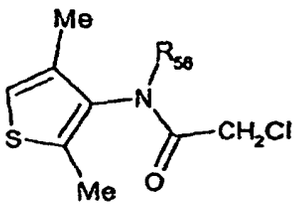
R_{51} CH_2-OMe, Ethyl oder Wasserstoff ist,

R_{52} Wasserstoff ist oder R_{51} und R_{52} zusammen die Gruppe -CH=CH-CH=CH- sind; und einer Verbindung der Formel 2.2



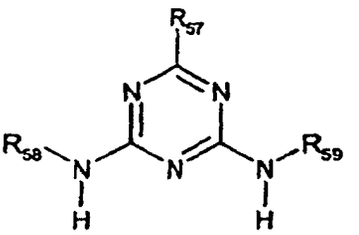
(2.2),

worin
R_{53} Ethyl ist,
R_{54} Methyl oder Ethyl ist, und
R_{55} -CH(Me)-CH_2OMe, <S>-CH(Me)-CH_2OMe, CH_2OMe oder CH_2O-CH_2CH_3 ist; und einer Verbindung der Formel 2.3



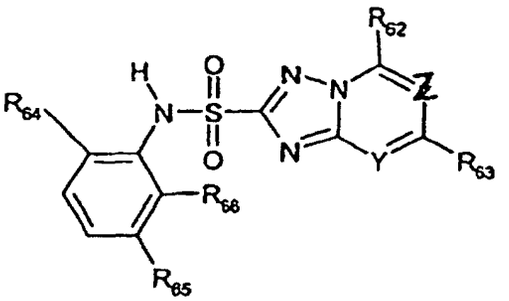
(2.3),

worin
R_{56} CH(Me)-CH_2OMe oder <S>CH(Me)-CH_2OMe ist;
einer Verbindung der Formel 2.4



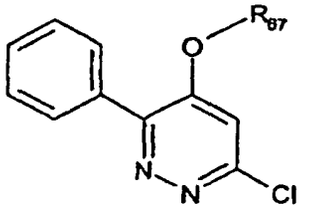
(2.4),

worin
R_{57} Chlor, Methoxy oder Methylthio ist,
R_{58} Ethyl ist, und
R_{59} Ethyl, Isopropyl, -C(CN)(CH_3)-CH_3 oder tert-Butyl ist;
und einer Verbindung der Formel 2.6

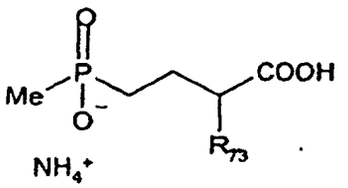


(2.6),

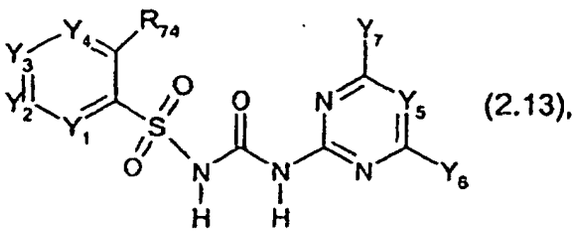
worin
R_{62} Wasserstoff, Methoxy oder Ethoxy ist,
R_{63} Wasserstoff, Methyl, Methoxy oder Fluor ist,
R_{64} COOMe, Fluor oder Chlor ist,
R_{65} Wasserstoff oder Methyl ist,
Y Methin, C-F oder Stickstoff ist,
Z Methin oder Stickstoff ist, und
R_{66} Fluor oder Chlor ist;
und einer Verbindung der Formel 2.7


(2.7),

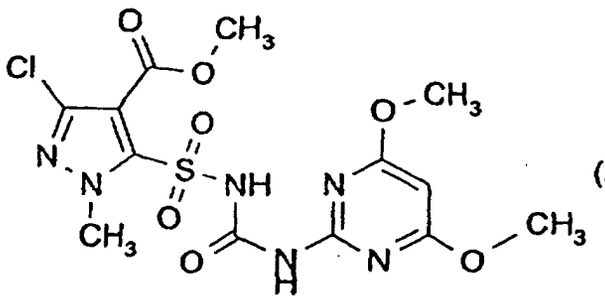
worin
R_{67} Wasserstoff oder -C(O)-S-n-Octyl ist;
und einer Verbindung der Formel 2.12


(2.12),

worin
R_{73} NH_2 oder <S>NH_2 ist;
einer Verbindung der Formel 2.13

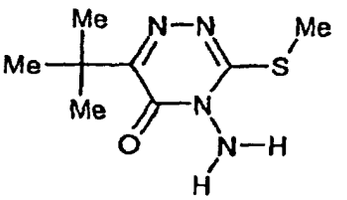

(2.13),

worin
Y_1 Stickstoff Methin, NH-CHO oder N-Me ist,
Y_2 Stickstoff, Methin oder C-I ist,
Y_3 Methin ist,
Y_4 Methin ist oder Y_3 und Y_4 zusammen Schwefel oder C-Cl sind,
Y_5 Stickstoff oder Methin ist,
Y_6 Methyl, Difluormethoxy, Trifluormethyl oder Methoxy ist,
Y_7 Methoxy oder Difluormethoxy ist, und
R_{74} $CONMe_2$, COOMe, $COOC_2H_5$, Trifluormethyl, CH_2-CH_2CF_3 oder $S0_2CH_2CH_3$ ist, oder ein Natriumsalz davon;
und der Verbindung der Formel 2.13c



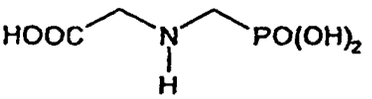
(2.13.c),

und der Verbindung der Formel 2.14



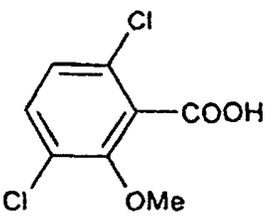
(2.14),

und der Verbindung der Formel 2.16



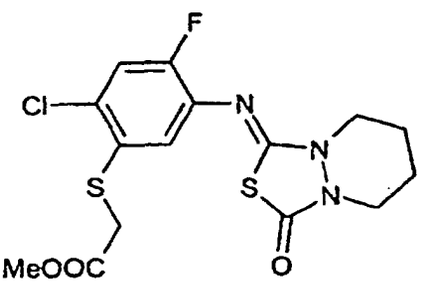
(2.16),

und der Verbindung der Formel 2.19



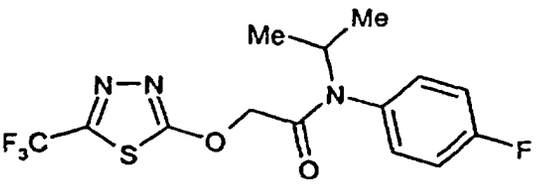
(2.19),

und der Verbindung der Formel 2.25



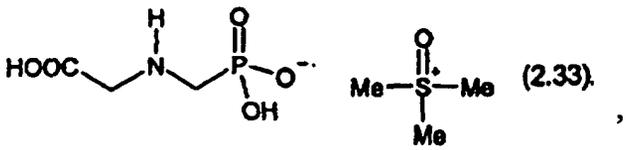
(2.25),

und der Verbindung der Formel 2.30



(2.30)

und der Verbindung der Formel 2.33



(2.33),

umfaßt.

2. Verfahren zur Bekämpfung des unerwünschten Pflanzenwachstums in Früchten von Nutzpflanzen, das es ermöglicht, daß eine herbizid wirksame Menge einer Zusammensetzung nach Anspruch 1 auf der Nutzpflanze oder ihrem Genort agiert.

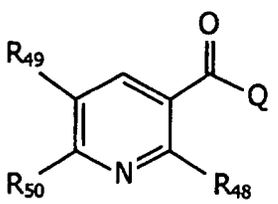
3. Verfahren nach Anspruch 2, wobei die Nutzpflanze Mais oder Zuckerrohr ist.

4. Verfahren nach Anspruch 2, wobei die Früchte von Nutzpflanzen mit der genannten Zusammensetzung bei Ausbringungsmengen, die einer Gesamtmenge des Wirkstoffes von 1 bis 5000 g pro Hektar entsprechen, behandelt werden.

Revendications

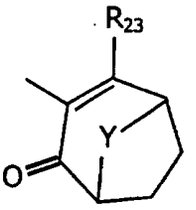
1. Composition sélective du point de vue herbicide qui, en plus de comprendre des adjuvants de formulation inertes habituels, comprend comme ingrédient actif un mélange constitué

   a) d'une quantité efficace du point de vue herbicide d'un composé de formule Ia



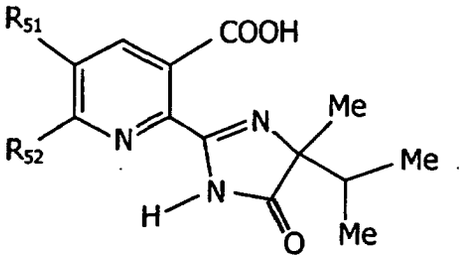
(Ia)

   dans laquelle
   R_{48} est un alkyle en C_1-C_6, un alcényle en C_2-C_6, un haloalcényle en C_2-C_6, un alcynyle en C_2-C_6, un haloalcynyle en C_2-C_6, un cycloalkyle en C_3-C_6 ou un haloalkyle en C_1-C_6;
   R_{49} est un hydrogène, un alkyle en C_1-C_6, un haloalkyle en C_1-C_6, un halogène ou un phényle qui peut être substitué par un alkyle en C_1-C_3, un haloalkyle en C_1-C_3, un alcoxy en C_1-C_3, un haloalcoxy en C_1-C_3, un halogène, un cyano ou par un nitro ;
   R_{50} est un haloalkyle en C_1-C_6 ; et
   Q est le groupe Q_2



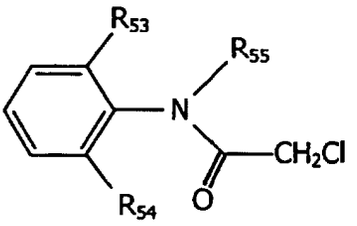
(Q_2),

dans lequel R_{23} est un hydroxy et
Y est un oxygène, un soufre, une liaison chimique ou un pont alkylène en C_1-C_4 ; ou d'un sel acceptable du point de vue agronomique d'ùn tel composé et
b) d'une quantité efficace de façon synergétique d'un ou plusieurs composés choisis entre un composé de formule 2.1



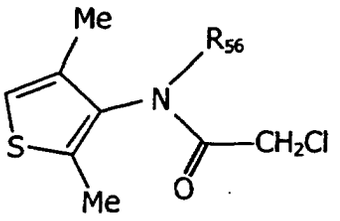
(2.1),

dans laquelle R_{51} est CH_2-OMe, un éthyle ou un hydrogène ;
R_{52} est un hydrogène ou bien R_{51} et R_{52} constituent ensemble le groupe -CH=CH-CH=CH- ;
et un composé de formule 2.2



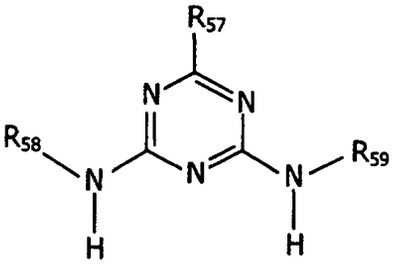
(2.2),

dans laquelle R_{53} est un éthyle, R_{54} est un méthyle ou un éthyle et R_{55} est -CH(Me)-CH_2OMe, <S>-CH(Me) -CH_2OMe, CH_2OMe ou CH_2O-CH_2CH_3;
et un composé de formule 2.3



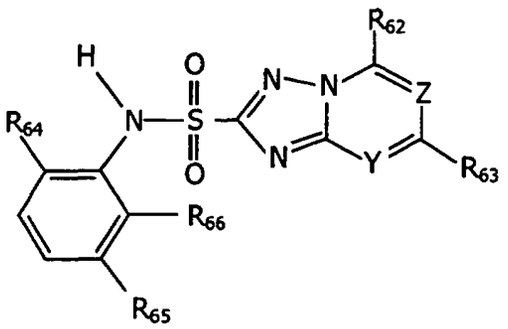
(2.3),

dans laquelle R_{56} est CH(Me)-CH_2OMe ou <S>CH(Me)-CH_2OMe ; un composé de formule 2.4



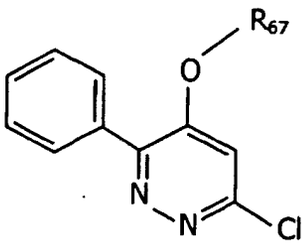
(2.4),

dans laquelle R_{57} est un chlore, un méthoxy ou un méthylthio, R_{58} est un éthyle et R_{59} est un éthyle, un isopropyle -C(CN)(CH_3)-CH_3 ou un *tert*-butyle ;
et un composé de formule 2.6



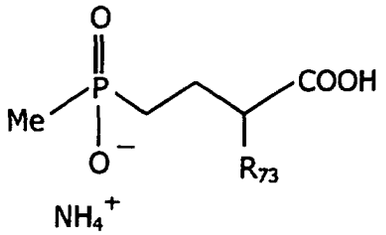
(2.6),

dans laquelle R_{62} est un hydrogène, un méthoxy ou un éthoxy, R_{63} est un hydrogène, un méthyle, un méthoxy ou un fluor, R_{64} est COOMe, un fluor ou un chlore, R_{65} est un hydrogène ou un méthyle, Y est un méthine, C-F ou un azote, Z est un méthine ou un azote et R_{66} est un fluor ou un chlore ; et un composé de formule 2.7



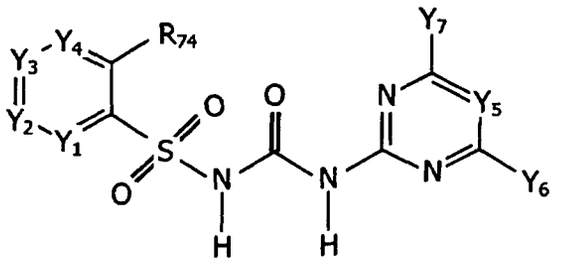
(2.7),

dans laquelle R_{67} est un hydrogène ou -C(O)-S-*n*-octyle;
et un composé de formule 2.12



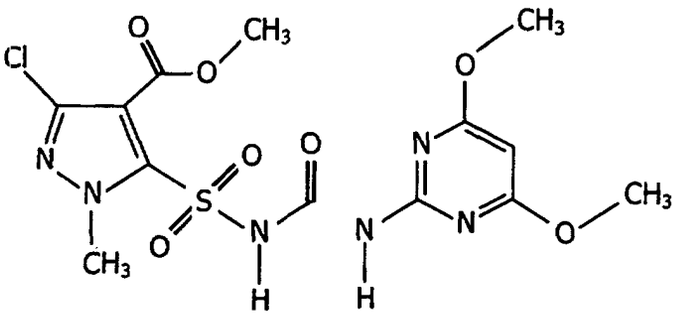
(2.12),

dans laquelle R_{73} est NH_2 ou <S>NH_2 ;
et un composé de formule 2.13



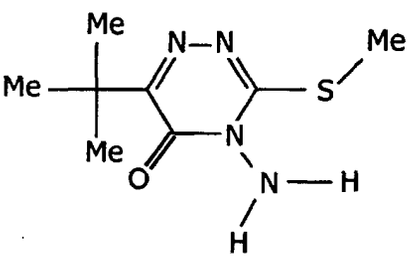
(2.13),

dans laquelle Y_1 est un azote, un méthine, NH-CHO ou N-Me, Y_2 est un azote, un méthine ou C-I, Y_3 est un méthine, Y_4 est un méthine ou bien Y_3 et Y_4 sont ensemble un soufre ou C-Cl, Y_5 est un azote ou un méthine, Y_6 est un méthyle, un difluorométhoxy, un trifluorométhyle ou un méthoxy, Y_7 est un méthoxy ou un difluorométhoxy et R_{74} est $CONMe_2$, COOMe, $COOC_2H_5$, un trifluorométhyle, CH_2-CH_2CF_3 ou $SO_2CH_2CH_3$ ou un sel de sodium de celui-ci ; et le composé de formule 2.13.c



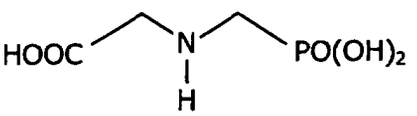
(2.13.c),

et le composé de formule 2.14



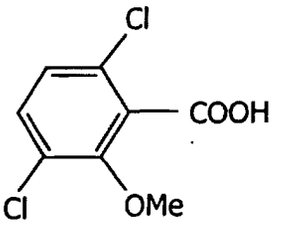
(2.14),

et le composé de formule 2.16



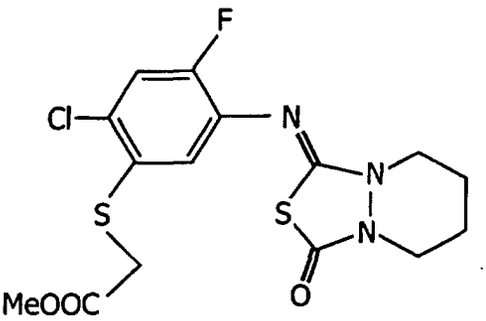
(2.16),

et le composé de formule 2.19



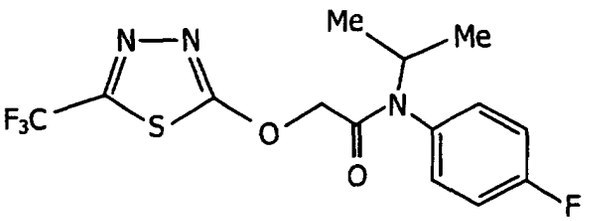
(2.19),

et le composé de formule 2.25



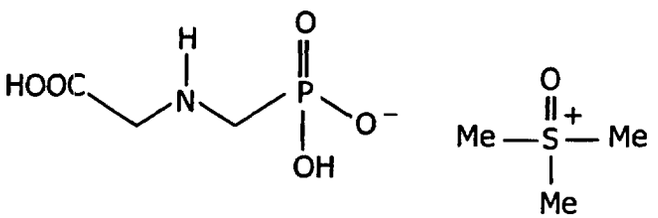
(2.25),

et le composé de formule 2.30



(2.30),

et le composé de formule 2.33



(2.33).

2. Procédé de lutte contre la croissance de plantes non souhaitées dans des cultures de plantes utiles, lequel comprend de laisser une quantité efficace du point de vue herbicide d'une composition selon la revendication 1 agir sur la plante de culture ou sur le lieu de celle-ci.

3. Procédé selon la revendication 2, dans lequel la plante de culture est du maïs ou de la canne à sucre.

4. Procédé selon la revendication 2, dans lequel les cultures de plantes utiles sont traitées avec la composition mentionnée à des taux d'application correspondant à une quantité totale d'ingrédient actif allant de 1 à 5000 g par hectare.