(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 May 2002 (02.05.2002)

PCT

(10) International Publication Number
WO 02/34048 A1

(51) International Patent Classification^7: **A01N 25/34**

(21) International Application Number: PCT/EP01/12187

(22) International Filing Date: 22 October 2001 (22.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2066/00 23 October 2000 (23.10.2000) CH

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: AGROCHEMICAL COMPOSITIONS WITH QUINOLINE SAFENERS

(57) Abstract: Agrochemical composition in the form of a concentrate comprising, in addition to customary formulation auxiliaries, a quinoline safener, wherein the quinoline safener has the formula (I) in which M is hydrogen, a mono-, di-or trivalent metal, ammonium, $N(R)_4$ or $HN(R)_3$, in which the radicals R are identical or different from each other and are C_1-C_{16}alkyl or C_1-C_{16}hydroxyalkyl, or M is $S(R_1)_3$ or $P(R_1)_4$,¿ ?in which the radicals R_1 are identical or different from each other and are C_1-C_{20}alkyl, C_1-C_{20}alkenyl, C_1-C_{20}alkynyl, aryl substituted by C_1-C_{20}alkyl, C_1-C_{20}alkenyl, C_1-C_{20}alkynyl or heteroaryl substituted by C_1-C_{20}alkyl, C_2-C_{20}alkenyl, C_2-C_{20}alkynyl or heteroaryl substituted by C_1-C_{20}alkyl, C_2-C_{20}alkenyl, C_2-C_{20}alkynyl, or 2 radicals R_1 together with the sulphur or phosphorus atom to which they are bonded form a 5- or 6-membered ring.

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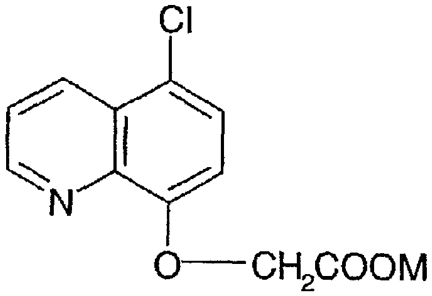
AGROCHEMICAL COMPOSITIONS WITH QUINOLINE SAFENERS

The present invention relates to novel agrochemical compositions in the form of concentrates comprising a quinoline safener.

Quinolines, their preparation and their action as safeners are known from a series of publications such as DE-A-2 546 845, US-A-3 351 525, Chem. Abstr. 79 (1973) 53154r and EP-A-94 349.

The present invention relates to agrochemical compositions in the form of concentrates comprising, in addition to customary formulation auxiliaries, a quinoline safener, wherein the quinoline safener has the formula



in which M is hydrogen, a mono-, di- or trivalent metal, ammonium, $N(R)_4$ or $HN(R)_3$, in which the radicals R are identical or different from each other and are C_1-C_{16}alkyl or C_1-C_{16}hydroxyalkyl, or M is $S(R_1)_3$ or $P(R_1)_4$, in which the radicals R_1 are identical or different from each other and are C_1-C_{20}alkyl, C_2-C_{20}alkenyl, C_2-C_{20}alkynyl, aryl substituted by C_1-C_{20}alkyl, C_2-C_{20}alkenyl, C_2-C_{20}alkynyl or heteroaryl substituted by C_1-C_{20}alkyl, C_2-C_{20}alkenyl or C_2-C_{20}alkynyl, or 2 radicals R_1 together with the sulphur or phosphorus atom to which they are bonded form a 5- or 6-membered ring.

The metal atoms M which may be present in the quinoline safeners of the formula I are preferably those of the alkali metals and alkaline earth metals, in particular sodium, potassium, calcium, magnesium and, in particular, aluminium and iron as preferred representatives of trivalent metals.

Preferred among the alkyl and hydroxyalkyl radicals R are those having 12 to 16 carbon atoms and also those having 1 to 4 carbon atoms. The radicals $N(R)_4$ and $HN(R)_3$ especially preferably comprise a long-chain and 2 or 3 short-chain alkyl radicals such as, for example, hexadecyltriethylammonium, tetradecyltriethylammonium, dodecyltriethylammonium, dodecylethyldimethylammonium and furthermore tetradodecylammonium. Preferred alkyl radicals R_1 comprise 1 to 12, in particular 1 to 6, carbon atoms. The alkyl radicals R and R_1 can be substituted further, for example by halogen, alkoxy or haloalkoxy, preferably having in each case 1 to 4 carbon atoms. Preferred alkenyl and alkynyl radicals R_1 comprise 2 to 12 carbon atoms. They can comprise more than one unsaturated bond and can be substituted by halogen, alkoxy or haloalkoxy, preferably having in each case 1 to 4 carbon atoms. Suitable examples of aryl radicals R_1 are phenyl, naphthyl, tetrahydronaphthyl, indanyl and indenyl, with phenyl being preferred. These radicals can be substituted by the abovementioned alkyl, alkenyl and alkynyl radicals. Heteroaryl radicals R_1 which must preferably be mentioned are 5- and 6-membered rings which comprise in particular nitrogen and/or oxygen atoms such as, for example, pyridyl, pyrimidinyl, triazinyl, thienyl, thiazolyl, pyrazolyl, imidazolyl, piperidyl, dioxolanyl, morpholinyl and tetrahydrofuryl. These heterocycles too can be substituted further by the abovementioned alkyl, alkenyl and alkynyl radicals. In each case 2 radicals R_1 together with the sulphur or phosphorus atom to which they are bonded may form a ring. Preferably, 5- or 6-membered rings which are saturated are formed in this process. The sulphonium and phosphonium cations which can be used in accordance with the invention are described, for example, in WO 00/44227.

Preferred agrochemical compositions of the present invention comprise a quinoline safener of the formula I in which M is hydrogen, sodium, potassium or tri(hydroxyethyl)ammonium.

A further group of preferred agrochemical compositions comprise a quinoline safener of the formula I in which M is calcium, magnesium, aluminum, iron, trimethylsulphonium, triphenylsulphonium, tetraphenylphosphonium, triphenylmethylphosphonium, triphenylbenzylphosphonium, C_{12}-C_{16}alkyltrimethylammonium, C_{12}-C_{16}alkyltriethylammonium, tetramethylammonium, trimethylhydroxyethyleneammonium, tetradodecylammonium or dodecylethyldimethylammonium.

The compositions according to the invention have the advantage that the salts of the formula I have very high melting points compared with the corresponding esters, which is very valuable in terms of formulation. The salts can be incorporated into this type of formulation at a higher concentration than this would have been possible with the esters. The good solubility of the salts in water is also useful; depending on the choice of the cation, it can even be controlled specifically.

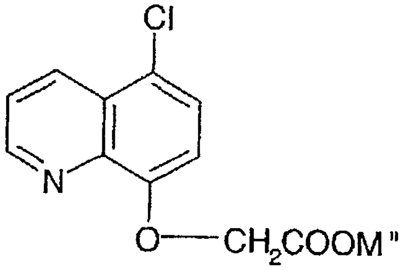
The safeners of the formula I can be prepared by customary methods, for example by reacting the corresponding methyl ester or 1-methylhexyl ester, both of which are known from EP-A-94 349, with an equimolar amount of a metal hydroxide in alcoholic solution at room temperature.

In this manner, the salts listed in the table which follows can be obtained.

Table 1: Compounds of the formula I

Compound No.	M	M.p. (°C)
1.01	Na	>250
1.02	K	>265
1.03	Ca	
1.04	Mg	
1.05	NH_4	227-228
1.06	$NH(CH_2CH_2OH)_3$	132-152
1.07	$N(CH_3)_4$	
1.08	$N(C_{12}H_{25})_4$	
1.09	$N(C_{12}H_{25})(C_2H_5)(CH_3)_2$	
1.10	$N(C_{12}H_{25})(CH_3)_3$	
1.11	$N(C_{12}H_{25})(C_2H_5)_3$	
1.12	$N(CH_3)_3(CH_2CH_2OH)$	
1.13	Al	
1.14	Fe	
1.15	H	232-233
1.16	$S(CH_3)_3$	
1.17	$S(C_6H_5)_3$	
1.18	$P(C_6H_5)_4$	
1.19	$P(C_6H_5)_3CH_3$	
1.20	$P(C_6H_5)_3CH_2C_6H_5$	

The safeners of the formula II



II,

in which M" is calcium, magnesium, aluminium, iron, trimethylsulphonium, triphenylsulphonium, tetraphenylphosphonium, triphenylmethylphosphonium, triphenylbenzylphosphonium, C_{12}-C_{16}alkyltrimethylammonium, C_{12}-C_{16}alkyltriethylammonium, tetradodecylammonium or dodecylethyldimethylammonium are novel and also a subject of the present invention.

The compositions according to the invention may additionally comprise a herbicide. This preferably takes the form of a representative selected from the group of the sulphonylureas, sulphonamides, imidazolinones, carbazones, aryloxyphenoxypropionates, cyclohexanediones, arylcarboxylic acids and aryloxycarboxylic acids.

Herbicides which are particularly suitable for the combination with the safeners of the formula I are, in particular, sulphonylureas, preferably triasulfuron, tribenuron, metsulfuron, thifensulfuron, flupyrsulfuron, iodosulfuron, rimsulfuron, nicosulforon, cinosulfuron, bensulfuron, trifloxysulfuron and analogues, furthermore sulphonamides, preferably flumetsulam, metosulam, chloransulam, florasulam and analogues, and imidazolinones, preferably imazethabenz, imazethapyr, imazaquin, imazamox and analogues, and also carbazones, preferably flucarbazone, propoxycarbazone, amicarbazone and analogues, furthermore aryloxyphenoxypropionates, preferably clodinafop, fenoxaprop, diclofop, propaquizafop, quizalofop, fluazifop, cyhalofop, haloxyfop and analogues, and cyclohexanediones, preferably sethoxydim, clethodim, tralkoxydim and analogues and arylcarboxylic acids, preferably dicamba and clopyralid, oxopyrazolin derivatives as they are known from WO 99/47525, and aryloxycarboxylic acids, preferably 2,4-D, mecoprop, fluroxypyr and analogues, furthermore amicarbazone, azafenidin, benfluamid, benzfendizone, benzobicyclon, cinidon-ethyl, diclosulam, fentrazamid, flufenacet, flufenpyr, foramsulfuron, indanofan, mesosulfuron, mesotrione, oxaziclomefone, penoxsulam, pethoxamid, picolinafen, profoxidim, profluazol, propoxycarbazone, pyraflufen, pyrazogyl, sulfosulfuron, tepraloxydim and tritosulfuron.

For application, the safeners of the formula I, if appropriate together with a herbicide, are expediently processed together with the auxiliaries conventionally used in the art of formulation to give agrochemical compositions in the form of concentrates, for example emulsion concentrates (EC, EW and SL), suspension concentrates (SC), capsule suspensions (CS), flowables (FW and OF), powders (SP) or granules (WP, WG, SG and DG), concentrates of the WP, WG, SG and SC types being preferred. The abbreviations used herein correspond to the international names of unformulated and formulated pesticides given in the Manual on Development and Use of FAO Specifications for Plant Protection Products, Fifth edition, January, 1999, pages 144 et seq. The compositions according to the invention are prepared in the known manner, for example by intimately mixing and/or grinding the active substances together with liquid or solid formulation auxiliaries such as, for example, solvents or solid carriers. Furthermore, surface-active compounds (surfactants) may additionally be used when preparing the formulations.

The following can be suitable as solvents: aromatic hydrocarbons, preferably the fractions C_8 to C_{12}, such as, for example, xylene mixtures or substituted naphthalenes, phthalic esters such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons such as cyclohexane or paraffins, alcohols such as ethanol, 2-ethylhexanol, oleyl alcohol, n-octanol, isotridecanol, cyclohexanol, tetrahydrofuryl alcohol and glycols such as ethylene glycol, dipropylene glycol, hexylene glycol, and also their ethers and esters such as butyl lactate, triethyl citrate, ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, isobornyl acetate, amyl acetate, benzyl acetate, methyl benzoate, ketones such as cyclohexanone, acetophenone, butyrolactone, diacetone alcohol, strongly polar solvents such as N-methyl-2-pyrrolidone, N-octylpyrrolidone, dimethyl sulphoxide or N,N-dimethylformamide, and epoxidized or unexpoxidized vegetable oils such as tallow oil, coconut oil, rapeseed oil or soya oil; or water. The solvents which are available under the trade names Exxsol D-80 ®, Edenor ME-SU®, Edenor ME C6-10®, Emery 2231®, Polyglycol P 1200E®, Exxate 700®, Exxate 900®, Exxate 1000®, Atplus®, Solvesso 150®, Solvesse 200®, Benzoflex 9-88®, Genagen 4166® are furthermore also suitable.

Materials which are used for solid carriers, for example for dusts and dispersible powders, are, as a rule, ground natural minerals such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties of the formulation, highly disperse silica or highly disperse absorbent polymers may also be added. Suitable particulate, adsorptive carriers for granules are porous types such as, for example, pumice, crushed bricks, sepiolite or bentonite, and suitable non-absorptive carrier materials are, for example, calcite or sand. Urea/formaldehyde condensates and melamine/formaldehyde condensates are also proven solid carriers. In addition, a multiplicity of pregranulated materials of inorganic or organic origin may also be used, such as, in particular, dolomite or comminuted plant residues.

Suitable surface-active compounds are, depending on the type of the active substance of the formula I to be formulated, nonionic, cationic and/or anionic surfactants and surfactant mixtures with good emulsifying, dispersing and wetting properties.

Suitable anionic surfactants may be not only what are known as water-soluble soaps, but also water-soluble synthetic surface-active compounds.

Soaps which may be mentioned are the alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts of higher fatty acids (C_{10}-C_{22}) such as, for example, the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which can be obtained from, for example, coconut oil or tallow oil. The fatty acid methyltaurinates may also be mentioned.

However, what are known as synthetic surfactants, in particular fatty alcohol sulphonates, fatty alcohol sulphates, sulphonated benzimidazole derivatives or alkylarylsulphonates, are used more frequently.

As a rule, the fatty alcohol sulphonates or fatty alcohol sulphates are present as alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts and have an alkyl radical of 8 to 22 carbon atoms, alkyl also including the alkyl moiety of acyl radicals, for example the sodium or calcium salt of lignosulphonic acid, of the dodecylsulphuric ester or of a fatty alcohol sulphate mixture prepared from natural fatty acids. They also include the salts of the sulphuric esters and sulphonic acids of fatty alcohol/ethylene oxide adducts. The sulphonated benzimidazole derivatives preferably comprise 2 sulpho groups and one fatty acid residue of 8-22 carbon atoms. Alkylarylsulphonates are, for example, the sodium, calcium or triethanolamine salts of dodecylbenzenesulphonic acid, of dibutylnaphthalenesulphonic acid or of a naphthalenesulphonic acid/formaldehyde condensate.

Other suitable compounds are the corresponding phosphates such as, for example, the salts of the phosphoric ester of a p-nonylphenol (4-14)-ethylene oxide adduct, or phospholipids.

Examples of nonionic surfactants which may be mentioned are polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols which may comprise 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols. Further suitable nonionic surfactants are the water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol and alkyl polypropylene glycol with 1 to 10 carbon atoms in the alkyl chain which comprise 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. The abovementioned compounds customarily comprise 1 to 5 ethylene glycol units per propylene glycol unit.

Examples of nonionic surfactants which may be mentioned are nonylphenolpolyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol.

Other substances which are suitable are fatty acid esters of polyoxyethylenesorbitan, such as polyoxyethylenesorbitan trioleate.

The cationic surfactants are mainly quaternary ammonium salts which comprise at least one alkyl radical having 8 to 22 carbon atoms as N-substituents and which have lower halogenated or free alkyl, benzyl or lower hydroxyalkyl radicals as further substituents. The salts are preferably in the form of halides, methylsulphates or ethylsulphates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The surfactants conventionally used in the art of formulation are described, inter alia, in the following publications: "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch" [surfactant guide], Carl Hanser Verlag, Munich/Vienna, 1981, and M. and J. Ash, "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-81.

As a rule, the agrochemical preparations according to the invention comprise 0.1 to 99% by weight, in particular 0.1 to 95% by weight, of safener, if appropriate together with the herbicide, 1 to 99.9% by weight of a solid or liquid formulation auxiliary and 0 to 25% by weight, in particular 0.1 to 25% by weight, of a surfactant.

The compositions may also comprise further additives such as stabilizers, for example unepoxidized or epoxidized vegetable oils (epoxidized coconut oil, rapeseed oil or soya oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders, stickers and fertilizers and other active substances.

The invention also relates to a method for the selective control of weeds in crops of useful plants, which consists in treating the useful plants, their seeds or cuttings or the area on which they are grown with a herbicidally effective amount of the herbicide and a herbicide-antagonistically effective amount of the safener of the formula I, either simultaneously or separately.

The areas on which they are grown are understood as meaning the expanses of soil which support the growth of the crop plants or on which the seed of these crop plants has been sown, and also the soils on which these crop plants are intended to grow.

Suitable crop plants which can be protected against the damaging effect of the abovementioned herbicides by the safeners of the formula I are, in particular, cereals, maize, sorghum and millet species, rice, and also sugarcane, useful grasses and ornamental grasses, and soyabeans, cotton, sugarbeet and other broad-leaved crops. Crops are also to include those which have been made tolerant to herbicides or classes of herbicides by conventional plant breeding methods or by recombinant methods.

The weeds to be controlled can be monocotyledonous and dicotyledonous weeds such as, for example, Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Poa, Phalaris, Alopecurus, Sorghum halepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola, Lamium, Veronica and Cynodon.

Depending on the intended use, a safener of the formula I may be employed for pretreating the seed of the crop plant (dressing of the seed or of the cuttings) or incorporated into the soil before or after sowing. However, it may also be applied after emergence of the plants, either alone or together with the herbicide. The treatment of the plants or of the seed with the safener can therefore take place in principle independently of the point in time of application of the herbicide. However, the plants may also be treated by applying herbicide and safener simultaneously (for example as a tank mix). In accordance with the invention, safener and herbicide may be present in separate concentrates, but also in a single concentrate.

Prior to use, the concentrates are treated with customary diluents, such as, for example, water, oils or liquid fertilizers or mixtures of these. In addition, adjuvants may also be used, such as, for example, nonionic surfactants, mixtures of nonionic surfactants, mixtures of anionic surfactants with nonionic surfactants, cationic surfactants, organosilicon surfactants, mineral oil derivatives with or without surfactants, vegetable oil derivatives with or without addition of surfactants, alkylated derivatives of oils of vegetable or mineral origin with or without surfactants, fish oils and other animal oils of animal origin and their alkyl derivatives with or without surfactants, naturally occurring higher fatty acids, preferably those having 8 to 28 carbon atoms, and their alkyl ester derivatives, organic acids comprising an aromatic ring system and one or more carboxyl residues, and their alkyl derivatives, furthermore suspensions of vinyl acetate polymers or vinyl acetate/acrylic ester copolymers, mixtures of individual adjuvants with each other and in combination with organic solvents may lead to a further increase in the effect. Examples of nonionic surfactants which are suitable are polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which may preferably comprise 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols. Further suitable nonionic surfactants are the polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol and alkyl polypropylene glycol with, preferably, 1 to 10 carbon atoms in the alkyl chain which are soluble in water and preferably comprise 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. The abovementioned compounds customarily comprise 1 to 5 ethylene glycol units per propylene glycol unit. Further examples of nonionic surfactants which may also be mentioned are nonylphenolpolyethoxyethanols, castor oil polyethylene glycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Also suitable are fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate. Preferred among anionic surfactants are mainly alkyl sulphates, alkylsulphonates, alkylarylsulphonates, alkylated phosphoric acids, and their ethoxylated derivatives. The alkyl radicals usually comprise 8 to 24 carbon atoms. Preferred nonionic surfactants are known under the following commercial names: polyoxyethylene cocoalkylamine (for example AMIET® 105 (Kao Co.)), polyoxyethylene oleylamine (for example AMIET® 415 (Kao Co.)), nonylphenol polyethoxyethanols, polyoxyethylene stearylamine (for example AMIET® 320 (Kao Co.)), N-polyethoxyethylamines (for example GENAMIN® (Hoechst AG)), N,N,N',N'-tetra(polyethoxypolypropoxyethyl)ethylenediamines (for example TERRONIL® and TETRONIC® (BASF Wyandotte Corp.)), BRIJ® (Atlas Chemicals), ETHYLAN® CD and ETHYLAN® D (Diamond Shamrock), GENAPOL® C, GENAPOL® O, GENAPOL® S and GENAPOL® X080 (Hoechst AG), EMULGEN® 104P, EMULGEN® 109P and EMULGEN® 408 (Kao Co.); DISTY® 125 (Geronazzo), SOPROPHOR® CY 18 (Rhone Poulenc S.A.); NONISOL® (Ciba-Geigy), MRYL® (ICI); TWEEN® (ICI); EMULSOGEN® (Hoechst AG); AMIDOX® (Stephan Chemical Co.), ETHOMID® (Armak Co.); PLURONIC® (BASF Wyandotte Corp.), SOPROPHOR® 461P (Rhône Poulenc S.A.), SOPROPHOR® 496/P (Rhone Poulenc S.A.), ANTAROX FM-63 (Rhone Poulenc S.A.), SLYGARD 309 (Dow Corning), SILWET 408, SILWET L-7607N (Osi-Specialities). The cationic surfactants are mainly quaternary ammonium salts which comprise at least one alkyl radical having 8 to 22 carbon atoms as N-substituents and which have lower halogenated or free alkyl, benzyl or lower hydroxyalkyl radicals as further substituents. The salts are preferably in the form of halides, methylsulphates or ethylsulphates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide. The oils used are either of mineral or natural origin. The natural oils may also be of animal or vegetable origin. In the case of animal oils, materials which are preferred are mainly derivatives of beef tallow, but fish oils (for example sardine oil) and their derivatives are also used. Vegetable oils are in most cases seed oils of various origin. Examples which may be mentioned of vegetable oils which are used in particular are coconut oils, rapeseed oils or sunflower oils and their derivatives. Surfactants, oils, in particular vegetable oils, their derivatives such as alkylated fatty acids and their mixtures, for example with, preferably, anionic surfactants such as alkylated phosphoric acids, alkyl sulphates and alkylarylsulphonates and higher fatty acids which are conventionally used in the art of formulation and adjuvants and which can also be used in the compositions and spray mixtures according to the invention are described, inter alia, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1988, Stache, H., "Tensid-Taschenbuch" [surfactant guide], Carl Hanser Verlag, Munich/Vienna, 1990, M. and J. Ash, "Encyclopedia of Surfactants", Vol. I-IV, Chemical Publishing Co., New York, 1981-89, G. Kapusta, "A Compendium of Herbicide Adjuvants", Southern Illinois Univ., 1998,

L. Thomson Harvey, "A Guide to Agricultural Spray Adjuvants Used in the United States", Thomson Pubns., 1992. Preferred adjuvants are commercially available under the names Merge, Score, Actipron, Amigo, Emery, Edenor, Partna and Hasten.

The application rate of safener to herbicide to be applied depends largely on the type of application. In the case of a field treatment which is effected either using a tank mix with a combination of safener and herbicide or by applying safener and herbicide separately, the ratio of herbicide to safener is, as a rule, from 1:100 to 1:1, preferably 1:50 to 5:1.

In the case of a field treatment, the rates which are applied are, as a rule, 0.001 to 5.0 kg of safener/ha, preferably from 0.001 to 0.5 kg of safener/ha.

The application rates of herbicide are, as a rule, between 0.001 and 2 kg/ha, but preferably between 0.005 and 1 kg/ha.

The compositions according to the invention are suitable for all application methods which are conventionally used in agriculture, such as, for example, pre-emergence application, post-emergence application and seed dressing.

A variety of methods and techniques such as, for example, those given hereinbelow, are suitable for the use of safeners of the formula I or compositions comprising them for protecting crop plants against harmful effects of herbicides:

i) <u>seed dressing</u>

a) Dressing the seeds with a safener formulated as a wettable powder by shaking in a container until the seed surface is uniformly covered (dry seed treatment). Approximately 1 to 500 g of safener (4 g to 2 kg of wettable powder) are used per 100 kg of seed.

b) Dressing the seeds with an emulsion concentrate of the safener following method a) (liquid seed dressing).

c) Seed dressing by immersing the seed in a liquor comprising 100-1000 ppm of safener, preferably for 1 to 72 hours, which, if desired, is followed by drying the seeds (seed soaking). On occasions, just briefly immersing the seed will also suffice.

Dressing of the seed or treatment of the germinated seedling are naturally the preferred methods of application since the treatment with safener is directed entirely at the target crop. As a rule, 1 to 1000 g of safener, preferably 5 to 250 g of safener, are used per 100 kg of seed, but it is also possible to deviate from the limit concentrations stated in both directions, depending on the methodology, which also makes possible to addition of other active substances or micronutrients (repeated seed treatment).

ii) <u>application as tank mix</u>

A liquid preparation of a mixture of safener and herbicide (mutual quantitative ratio between 10:1 and 1:100) is used, the application rate of herbicide being 0.005 to 5.0 kg per hectare. Such tank mixes are applied before or after sowing.

iii) <u>application into the seed furrow</u>

The safener, in the form of an emulsion concentrate, wettable powder or granules, is introduced into the uncovered sown seed furrow. After the seed furrow has been covered, the herbicide is applied pre-emergence in the customary fashion.

iv) <u>controlled release of active substance</u>

The dissolved safener of the formula I is applied into mineral granule carriers or polymerized granules (urea/formaldehyde) and allowed to dry. If desired, a coating can be applied (coated granules) which permits slow release of the active substance over a specific period.

In particular, preferred formulations have the following composition: (active substance mixture = safener + herbicide; % = percent by weight)

<u>Emulsifiable concentrates:</u>

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

Suspension concentrates:
active substance 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 substance 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 substance mixture: 0.1 to 30%, preferably 0.1 to 15%
solid carrier: 99.5 to 70%, preferably 97 to 85%

Dispersible granules:
active substance 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%

The examples which follow illustrate the invention in greater detail without imposing any limitations.

Formulation examples of mixtures of herbicides and safener of the formula I
(active substance mixture = safener + herbicide; % = percent by weight)

F1. Emulsion concentrates	a)	b)	c)	d)
active substance mixture	5%	10%	25%	50%
calcium dodecylbenzenesulphonate	6%	8%	6%	8%
castor oil polyglycol ether (36 mol of EO)	4%	-	4%	4%
octylphenyl polyglycol ether (7-8 mol of EO)	-	4%	-	2%
Cyclohexanone	-	-	10%	20%
aromatic hydrocarbon mixture C_9-C_{12}	85%	78%	55%	16%

Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

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

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

F3. Wettable powder	a)	b)	c)	d)
active substance mixture	5%	25%	50%	80%
sodium lignosulphonate	4%	-	3%	-
sodium lauryl sulphate	2%	3%	-	4%
sodium diisobutylnaphthalenesulphonate	-	6%	5%	6%
octylphenyl polyglycol ether (7-8 mol of EO)	-	1%	2%	-
highly-disperse silica	1%	3%	5%	10%
kaolin	88%	62%	35%	-

The active substance is mixed thoroughly with the additives and ground thorougly in a suitable mill. This gives wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granules	a)	b)	c)
active substance mixture	0.1%	5%	15%
highly-disperse silica	0.9%	2%	2%
inorganic carrier (Ø 0.1–1 mm), e.g. $CaCO_3$ or SiO_2	99.0%	93%	83%

The active substance is dissolved in methylene chloride, the carrier is sprayed with the solution, and the solvent is subsequently evaporated in vacuo.

F5. Coated granules	a)	b)	c)
active substance mixture	0.1%	5%	15%
polyethylene glycol MW 200	1.0%	2%	3%
highly-disperse silica	0.9%	1%	2%
inorganic carrier (Ø 0.1–1 mm), e.g. $CaCO_3$ or SiO_2	98.0%	92%	80%

In a mixer, the finely ground active substance is applied uniformly to the carrier which has been moistened with polyethylene glycol. This gives rise to dust-free coated granules.

F6. Extruder granules	a)	b)	c)	d)
active substance mixture	0.1%	3%	5%	15%
sodium lignosulphonate	1.5%	2%	3%	4%
Carboxymethylcellulose	1.4%	2%	2%	2%
Kaolin	97.0%	93%	90%	79%

The active substance is mixed with the additives, ground and moistened with water. This mixture is extruded and subsequently dried in a stream of air.

F7. Dusts	a)	b)	c)
active substance mixture	0.1%	1%	5%
Talc	39.9%	49%	35%
Kaolin	60.0%	50%	60%

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

Preferred WP formulations according to the invention comprise 5-50% by weight of safener or safener + herbicide, 1-15% by weight of dispersant (for example lignosulphonates such as Attisol II, Ufoxan 3A), 0-30% by weight of wetter (for example isotridecanol EO8 such as Genapol X-080, Morwet EFW, Genapol LRO), 5-90% by weight of carrier (for example Pergopak M, sodium sulphate, diatomaceous earth, aluminium silicate, Sopropon TA 72).

F8. Suspension concentrates	a)	b)	c)	d)
active substance mixture	3%	10%	25%	50%
ethylene glycol	5%	5%	5%	5%
nonylphenyl polyglycol ether (15 mol of EO)	-	1%	2%	-
sodium lignosulphonate	3%	3%	4%	5%
Carboxymethylcellulose	1%	1%	1%	1%
37% aqeous 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%

The suspension concentrates a) to d) may also be free from ethylene glycol. If appropriate, they may additionally comprise, for example, 0.2% of xanthan gum.

Especially suitable SC formulations comprise 1 to 700 g/l of safener or herbicide + safener, 0-100 g/l of dispersant (for example Soprophor 3D33, Soprophor 4D384, Atlox 4913, Morwet D425), 0-30 g/l of wetter (for example Genapol X-080, Morwet EFW, Genapol LRO, sodium lauryl sulphate), 0-50 g/l of buffer (for example citric acid, lactic acid, sodium phosphates, sodium carbonate and sodium hydroxide), 0-100 g/l of antifreeze (for example propylene glycol, glycerols, sodium sulphate), 0-50 g/l of thickener (Kelzan S, Rheozan, Laponite BD, Thixosil, Aerosil 200, Attagel 50, Bentone 36), 0-50 g/l of of preservative (for example Proxel GXL, formalin, orthophenylphenol), 0-400 g/l of fillers (calcium carbonate, kaolin, diatomaceous earth, silicon dioxide) and 0-50 g/l of antifoam (for example Rhodosil 426 R, silicone oils, Fluowet 80 B).

F9. Dispersible granules	a)	b)	c)	d)
active substance mixture	5%	25%	50%	80%
sodium lignosulphonate	4%	-	3%	-
sodium lauryl sulphate	2%	3%	-	4%
sodium diisobutylnaphthalenesulphonate	-	6%	5%	6%
octylphenyl polyglycol ether (7-8 mol of EO)	-	1%	2%	-
highly-disperse silica	1%	3%	5%	10%
kaolin	88%	62%	35%	-

The finely-ground active substance is mixed intimately with the additives. This gives a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

Water-soluble active substances such as, for example, the salts of the formula I according to the invention may also be formulated advantageously as SG formulations. These preferably comprise 0-50% by weight of the safener of the formula I in salt form, 0-20% by weight of dispersant (for example Morwet D425, Borresperse NA, Geropon TA72, Soprophor FL, Soprophor S40), 0-20% by weight of wetter (for example Morwet EFW, Tinovetin B, Genapol LRO), 0-5% by weight of antifoam (for example Rhodosil 426, Fluowet 80B) and 0-99% by weight of carrier (for example ammonium sulphate, sodium sulphate, kaolin, carbonates, diatomaceous earth).

Frequently, it is more convenient to formulate the active substance of the formula I and the herbicide individually and to combine them in water in the applicator in the desired mixing ratio shortly before application, for example in the form of a "tank mix".

The ability of the safeners of the formula I to protect crop plants from the phytotoxic effect of herbicides is illustrated in the examples which follow.

The examples which follow illustrate the invention in greater detail.

Example

Seeds of maize, barley and wheat are sown in a greenhouse in plastic pots comprising 0.5 l of garden soil. After the plants have emerged and reached the 2- to 3-leaf stage, a safener of the formula A and for comparison the known safener Cloquintocet-mexyl (The Pesticide Manual, 11th Edition (BCPC) 1997, No. 154) together with a herbicide are applied (as a readymix in the case of the safener of the formula I and clodinafop; as a tank mix in the case of the herbicides tralkoxydim, mesotrione, thifensulfuron, propoxycarbazone and florasulam). 20 days post-application, the protective action of the safener (in % phytotoxicity) is determined. As shown in Tables 2 to 8 hereinbelow, all of the safeners used are as or more effective than Cloquintocet-mexyl.

Table 2: Safener action on the herbicide of the formula A

	Herbicide (A) + Cloquintocet			Herbicide (A) + 1.15			Herbicide (A) + 1.01			Herbicide (A) + 1.02		
	500	250	125 g/ha	500	250	125 g/ha	500	250	125 g/ha	500	250	125 g/ha
Barley Manitou	20	10	10	5	0	0	20	10	0	0	0	0

The herbicide of the formula A is 2,2-dimethylpropionic acid 8-(2,6-diethyl-4-methylphenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepin-7-yl ester.

The herbicide/safener mixture was employed as WG 24

Table 3: Safener action on clodinafop

	Clodinafop + Cloquintocet			Clodinafop + 1.15			Clodinafop + 1.01			Clodinafop + 1.02		
	240	120	60 g/ha	240	120	60 g/ha	240	120	60 g/ha	240	120	60 g/ha
Barley Manitou	20	5	5	0	0	0	0	0	0	25	0	0

The herbicide/safener mixture was employed as WG 36

Table 4: Safener action on tralkoxydim

	Tralkoxydim +Cloquintocet 500+125 250+62.5 g/ha	Tralkoxydim + 1.15 500+88.5 250+44.25 g/ha	Tralkoxydim + 1.01 500+97 250+48.5 g/ha	Tralkoxydim + 1.02 500+102 250+51 g/ha
Wheat Arina	10	0	0	0
	10	0	0	0

Tralkoxydim was employed as SC 250, the safeners as WP 25

Table 5: Safener action on mesotrione

	Mesotrione + Cloquintocet 500+125 250+62.5 g/ha	Mesotrione + 1.15 500+88.5 250+44.25 g/ha	Mesotrione + 1.01 500+97 250+48.5 g/ha	Mesotrione + 1.02 500+102 250+51 g/ha
Maize Marista	5	5	0	5
	5	0	0	0

Mesotrione was employed as SC 100, the safeners as WP 25.

Table 6: Safener action on thifensulfuron

	Thifensulf. + Cloquintocet 100+50 25+12.5 g/ha	Thifensulf. + 1.15 100+17.5 50+8.75 g/ha	Thifensulf. + 1.01 100+19.5 50+9.75 g/ha	Thifensulf. + 1.02 100+20.5 50+10.25 g/ha
Wheat Arina	0	0	0	0
	0	0	0	0

Thifensulfuron was employed as WG 75, the safeners as WP 25.

Table 7: Safener action on propoxycarbazone

	Propoxyc. + Cloquintocet 250+50 100+25 g/ha	Propoxyc. + 1.15 200+35 100+17.5 g/ha	Propoxyc. + 1.01 200+39 100+19.5 g/ha	Propoxyc. + 1.02 200+41 100+20.5 g/ha
Wheat Arina	40	40	30	30
	25	30	30	30

Propoxycarbazone was employed as WG 70, the safeners as WP 25.

Table 8: Safener action on florasulam

	Florasulam + Cloquintocet 100+25 50+12.5 g/ha	Florasulam + 1.15 100+17.5 50+8.75 g/ha	Florasulam + 1.01 100+19.5 g/ha	Florasulam + 1.02 100+20.5 g/ha
Wheat Arina	30	30	20	15
	25	25		

Florasulam was employed as SC 50, the safener as WP 25.

In the readymix applications (Tables 2 and 3), the herbicide of the formula A and the safener were employed together in a WG 24. This formulation comprised 24% by weight of herbicide of the formula A, 6% by weight of safener, 10% by weight of Morwet, 5% by weight of Tinivetin B as wetter, 2% by weight of Geropon as dispersant, 1% by weight of silicone oil as antifoam and 12% by weight of carrier (10% by weight of Pergopak M, 5% by weight of anhydrous sodium sulphate, 7% by weight of Diatom 236 B). Clodinaflop together with the safeners was employed as WG 36. The WG 36 was composed as follows: 36.2% by weight of clodinafop, 7.8% by weight of safener 1.02 or 6.7% by weight of safener 1.15 or 6.8% by weight of safener 1.05 or 7.3% by weight of safener 1.01, 15% by weight of Ufoxane 3A as dispersant, 2% by weight of Geropon TA-72 as dispersant, 1% by weight of silicone oil as antifoam (Antifoam A TK 50) and 38% by weight of carrier (15% by weight of Pergopack M, 10% by weight of anhydrous sodium sulphate, remainder to 100% Diatom 236 B).

In general, WG formulations which are particularly suitable for the purposes of the present invention are those which comprise 1-45% by weight of herbicide + safener, 5-25% by weight of dispersant, 0-5% by weight of antifoam and 10-40% by weight of carrier.

However, the herbicide and safener may also be used as a formulation in accordance with Examples F1 to F9. Essentially the same results are obtained.

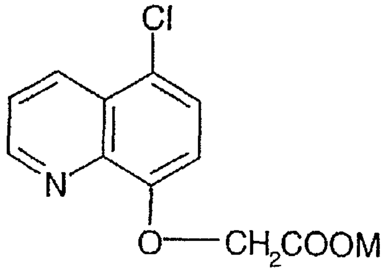
For application as a tank mix, (Tables 4 to 8), the safeners were used as WP25 in the following composition: 25% by weight of safener of the formula I or Cloquintocet, 5% of lignosulphonate (Attisol II), 1% of isotridecanol EO 8 (Genapol X-080), 5% of urea/formaldehyde condensate (Pergopack M), 3% of furandione/trimethylpentene polymer (Sopropon TA 72) and 61% of aluminium silicate (Kaolin Pulver AG).

Formulated as WG, SC or SG, essentially the same results are obtained. A typical SC formulation for the purposes of the present invention comprises: 400 g/l of safener 1.01, 1.02, 1.05 or 1.15, 20 g/l of dispersant Soprophor 4D384, 20 g/l of Genapol X-080, 5 g/l of buffer (citric acid), 60 g/l of antifreeze (propylene glycol), 2 g/l of thickener (Kelzan S), 0-50 g/l of preservative (Proxel GXL), 50 g/l of filler (kaolin), 5 g/l of antifoam (Rhodosil 426 R). A typical WG formulation according to the invention comprises 1-45% by weight of safener, 5-25% by weight of dispersent, 0-5% by weight of antifoam and 10-40% by weight of carrier, it being possible for the dispersent, the antifoam and the carrier to be identical to those of the SC formulation mentioned.

For the tank mix application, the remaining herbicides can be applied as outlined above for the herbicide of the formula A; however, as this applies with a view to the above experiments, they may also be used in their commercially available formulations.

WHAT IS CLAIMED IS:

1. An agrochemical composition in the form of a concentrate comprising, in addition to customary formulation auxiliaries, a quinoline safener, wherein the quinoline safener has the formula



I

in which M is hydrogen, a mono-, di- or trivalent metal, ammonium, $N(R)_4$ or $HN(R)_3$, in which the radicals R are identical or different from each other and are C_1-C_{16}alkyl or C_1-C_{16}hydroxyalkyl, or M is $S(R_1)_3$ or $P(R_1)_4$, in which the radicals R_1 are identical or different from each other and are C_1-C_{20}alkyl, C_2-C_{20}alkenyl, C_2-C_{20}alkynyl, aryl substituted by C_1-C_{20}alkyl, C_2-C_{20}alkenyl, C_2-C_{20}alkynyl or heteroaryl substituted by C_1-C_{20}alkyl, C_2-C_{20}alkenyl or C_2-C_{20}alkynyl, or 2 radicals R_1 together with the sulphur or phosphorus atom to which they are bonded form a 5- or 6-membered ring.

2. A composition according to claim 1, which comprises a quinoline safener of the formula I in which M is hydrogen, sodium, potassium or tri(hydroxyethyl)ammonium. .

3. A composition according to claim 1, which comprises a quinoline safener of the formula I in which M is calcium, magnesium, aluminum, iron, trimethylsulphonium, triphenylsulphonium, tetraphenylphosphonium, triphenylmethylphosphonium, triphenylbenzylphosphonium, C_{12}-C_{16}alkyltrimethylammonium, C_{12}-C_{16}alkyltriethylammonium, tetramethylammonium, trimethylhydroxyethyleneammonium, tetradodecylammonium or dodecylethyldimethylammonium.

4. A composition according to claim 1, which comprises a herbicide.

5. A composition according to claim 1, which comprises, as herbicide, a representative selected from the group consisting of the sulphonylureas, sulphonamides, imidazolinones, carbazones, aryloxyphenoxypropionates, cyclohexanediones, arylcarboxylic acids and aryloxycarboxylic acids.

6. A composition according to claim 1, wherein the concentrate is an SC, CS, EW, OF, FW, WG, SG, DG, SP, WP, EC or SL.

7. A composition according to claim 6, wherein the concentrate is an SC, WG, SG or WP.

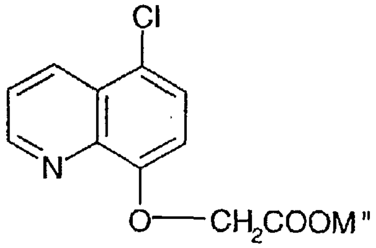
8. A method of controlling undesired plant growth, which comprises applying a composition according to claim 1 after dilution with customary diluents to the crop plants or their environment, independently of the point in time of application of a herbicide.

9. A method according to claim 8, wherein the diluents comprise adjuvants.

10. A method of controlling undesired plant growth, which comprises applying a herbicidally effective amount of a composition according to claim 4 after dilution with customary diluents to the crop plants or their environment.

11. A method according to claim 10, wherein the diluents comprise adjuvants.

12. A compound of the formula



II,

wherein M" is calcium, magnesium, aluminium, iron, trimethylsulphonium, triphenylsulphonium, tetraphenylphosphonium, triphenylmethylphosphonium, triphenylbenzylphosphonium, C_{12}-C_{16}alkyltrimethylammonium, C_{12}-C_{16}alkyltriethylammonium, tetramethylammonium, trimethylhydroxyethyleneammonium, tetradodecylammonium or dodecylethyldimethylammonium.

INTERNATIONAL SEARCH REPORT

Interr al Application No
PCT/EP 01/12187

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N25/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BIOSIS, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	GB 2 350 298 A (ZENECA LTD) 29 November 2000 (2000-11-29) page 12, line 8 -page 12, line 15; example 1; table 1	1,2,4-6
X	EP 0 094 349 A (CIBA GEIGY AG) 16 November 1983 (1983-11-16) cited in the application page 86 page 102 page 29, paragraph 2 claims	1,2,4-11

☐ *Further documents are listed in the continuation of box C.*

☒ *Patent family members are listed in annex.*

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 8 March 2002	Date of mailing of the international search report 18/03/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Donovan-Beermann, T

INTERNATIONAL SEARCH REPORT

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PCT/EP 01/12187

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