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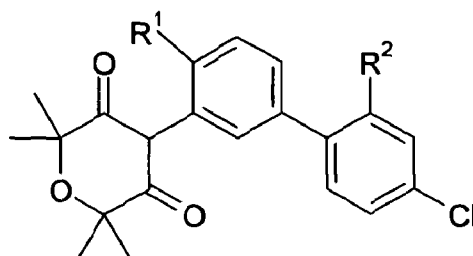
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(54) Title: HERBICIDAL COMPOSITION COMPRISING A PYRANDIONE HERBICIDE AND A SULFONYL UREA HERBICIDE



(I),

(57) Abstract: The invention relates to a herbicidal composition comprising: (a) a compound of formula (I) or an agriculturally acceptable salt thereof: wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine; and (b) metazosulfuron or an agriculturally acceptable salt thereof. Preferably, R<sup>1</sup> is ethyl and R<sup>2</sup> is chlorine; or R<sup>1</sup> is cyclopropyl and R<sup>2</sup> is fluorine. The invention also relates to a herbicidal composition comprising: the compound of formula (I) or a salt thereof, and halosulfuron-methyl or a salt thereof, wherein the weight ratio of the compound of formula (I) to the halosulfuron-methyl is from 30:60 to 250:3. The herbicidal compositions are preferably for controlling weeds in crops of useful plants (e.g. rice), especially for controlling Echinochloa, Brachiaria and/or other weeds. The invention also relates to a method of controlling Brachiaria weeds in crops of useful plants, which comprises applying the compound of formula (I) or an agriculturally acceptable salt thereof to the Brachiaria weeds or to the locus thereof.

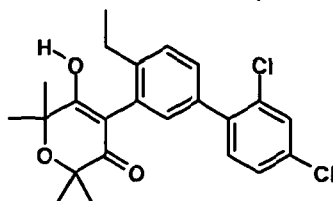
- 1 -

### Herbicidal composition comprising a pyrandione herbicide and a sulfonyl urea herbicide

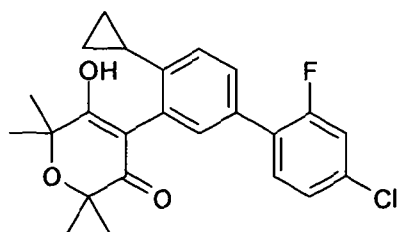
The present invention relates to a new herbicidal composition, for example suitable for  
5 controlling weeds (e.g. grassy weeds) in crops of useful plants, especially in crops of rice;  
which composition comprises a herbicidally active pyrandione [specifically, a 4-(substituted  
biphenyl-3-yl)-2,2,6,6-tetramethyl-2H-pyran-3,5(4H,6H)-dione; or more specifically, a 4-(4-  
ethyl or 4-cyclopropyl, 2'-chloro- or 2'-fluoro-, 4'-chloro-biphenyl-3-yl)-2,2,6,6-tetramethyl-2H-  
pyran-3,5(4H,6H)-dione], or an enol ketone tautomer thereof; and a sulfonyl urea herbicide.

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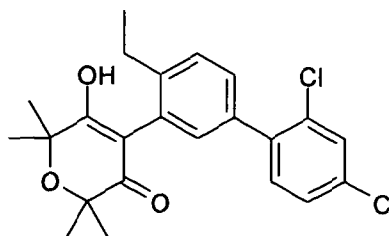
WO 2008/071405 A1 (Syngenta Participations AG and Syngenta Limited) discloses  
pyrandione, thiopyrandione and cyclohexanedione compounds, and enol ketone tautomer  
derivatives thereof, suitable for use as herbicides. WO 2008/071405 A1 also discloses  
mixtures of these pyrandione, thiopyrandione or cyclohexanedione compounds with any of a  
15 large number of herbicidal mixture partners. One of the many specific pyrandione herbicidal  
compounds disclosed in WO 2008/071405 A1 is compound A-45 whose structure is:



WO 2010/136431 A9 (Syngenta Limited) discloses a genus of spirocyclic epoxy ketones, and  
20 their use as intermediates in the preparation of herbicidally active substituted 4-phenyl-3,5-  
pyrandiones, 4-phenyl-3,5-thiopyrandiones and 6-phenylcyclohexane-1,3,5-triones including  
those disclosed in WO 2008/071405 A1. Two of the several specific pyrandione compounds  
disclosed in WO 2010/136431 A9 are Example P8 and Example P10, whose structures are  
shown below:



Example P8 from  
WO 2010/136431 A9

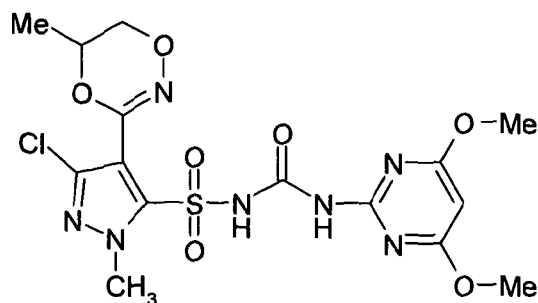


Example P10 from  
WO 2010/136431 A9

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- 2 -

Metazosulfuron (NC-620), whose CAS (Chemical Abstracts Service) registry number is 868680-84-6, is a herbicide of the sulfonyl urea class which has the following structure:



metazosulfuron

5

Metazosulfuron has the following chemical name: 3-chloro-4-(5,6-dihydro-5-methyl-1,4,2-dioxazin-3-yl)-*N*-[[4,6-dimethoxy-2-pyrimidinyl]amino]carbonyl]-1-methyl-1*H*-pyrazole-5-sulfonamide. Metazosulfuron may be used in the form of a salt (e.g. agriculturally acceptable salt) thereof. Metazosulfuron and its synthesis is disclosed as Compound no. 1 in Examples 1, 10, 11 and 12 on pages 18, 23 and 47 of EP 1 748 047 A1 (Nissan Chemical Industries, Ltd) which is derived from WO 2005/103044.

10

It is desirable to discover new mixtures of the pyrandione compounds or enol-ketone-tautomer-derivative compounds disclosed in WO 2008/071405 A1 with other co-herbicides, especially:

15

i) a mixture suitable for use in crops of rice, for example either transplanted flooded rice (e.g. using post-emergent application to the flood-waters) or direct-seeded rice (e.g. using post-emergent foliar and/or spray application), preferably having low or relatively low levels of phytotoxicity on the rice crops; and/or

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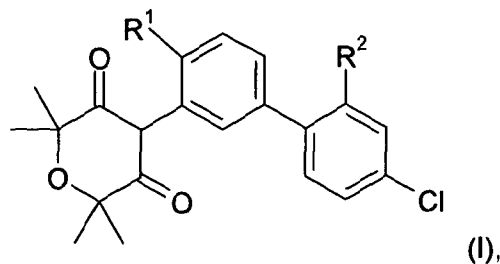
ii) mixtures suitable to control certain grassy weeds such as *Echinochloa* and/or *Brachiaria* which can be found in rice crops, while also having activity against certain sedges and/or certain broadleaf and/or dicotyledonous weeds which can be found in rice crops.

A **first aspect** of the present invention provides a herbicidal composition comprising:

25

(a) a compound of formula (I) or an agriculturally acceptable salt thereof:

- 3 -



wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine;

and

(b) metazosulfuron or an agriculturally acceptable salt thereof.

5

For example, the herbicidal composition typically comprises:

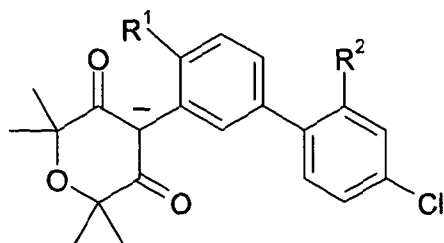
(a) a herbicidally effective amount of the compound of formula (I) or the agriculturally acceptable salt thereof, and

(b) a herbicidally effective amount of metazosulfuron or the agriculturally acceptable salt thereof.

10

Within the compound of formula (I), the C-H of the pyridone ring-carbon which is bonded to the biphenyl and which is between the two ketones, is acidic. Therefore, the agriculturally acceptable salt of the compound of formula (I) can, for example, be an agriculturally acceptable base addition salt such as an alkali metal (e.g. sodium, potassium or lithium) salt, alkaline earth (e.g. calcium or magnesium) salt, ammonium salt, or a tetraC<sub>1</sub>-C<sub>4</sub>alkylammonium (e.g. tetramethylammonium, tetra-ethyl-ammonium or tetra-n-butylammonium) salt thereof. For example, the anion of the base addition salt of the compound of formula (I) may, for example, have the following structure, where the negative charge is delocalized over the two diones and over the biphenyl:

20



Preferably, however, the compound of formula (I) is present as the free compound (e.g. as a substantially salt-free compound).

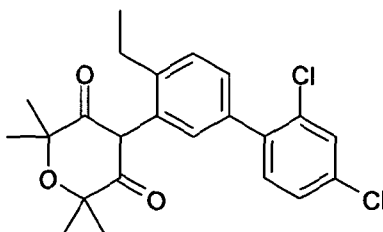
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In the compound of formula (I) or the salt thereof, in one preferred embodiment, R<sup>1</sup> is ethyl.

In the compound of formula (I) or the salt thereof, in an alternative preferred embodiment, R<sup>1</sup> is cyclopropyl.

5

In the compound of formula (I) or the salt thereof, in the most preferred embodiment, R<sup>1</sup> is ethyl and R<sup>2</sup> is chlorine. In this embodiment, which is most preferred, the compound of formula (I) is:



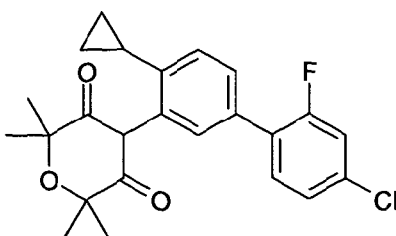
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(named Compound no. 1).

The above-shown compound has the following chemical name: 4-(2',4'-dichloro-4-ethylbiphenyl-3-yl)-2,2,6,6-tetramethyl-2H-pyran-3,5(4H,6H)-dione. Still more preferably, this compound or the salt thereof is present as the free compound (e.g. as a substantially salt-free compound). For the purposes of the present patent application and invention, the above-shown compound, present as the free compound, is named Compound no. 1. This compound (as the enol ketone tautomer) was previously disclosed as compound A-45 in WO 2008/071405 A1, and as Example P10 within WO 2010/136431 A9, and can in general be synthesized using the methods of preparation disclosed in either of these publications.

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In the compound of formula (I) or the salt thereof, in an alternative particularly preferred embodiment, R<sup>1</sup> is cyclopropyl and R<sup>2</sup> is fluorine. In this embodiment, which is particularly preferred, the compound of formula (I) is:



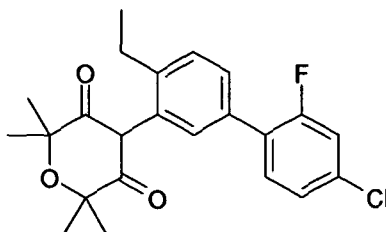
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(named Compound no. 2).

- 5 -

The above-shown compound has the following chemical name: 4-(4'-chloro-4-cyclopropyl-2'-fluorobiphenyl-3-yl)-2,2,6,6-tetramethyl-2*H*-pyran-3,5(4*H*,6*H*)-dione. Still more preferably, this compound or the salt thereof is present as the free compound (e.g. as a substantially salt-free compound). For the purposes of the present patent application and invention, the above-shown compound, present as the free compound, is named Compound no. 2. This compound (as the enol ketone tautomer) was previously disclosed as Example P8 within WO 2010/136431 A9, and can in general be synthesized using the methods of preparation disclosed in either WO 2008/071405 A1 or WO 2010/136431 A9.

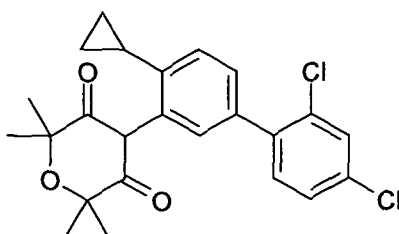
10 In the compound of formula (I) or the salt thereof, in an alternative embodiment, R<sup>1</sup> is ethyl and R<sup>2</sup> is fluorine. In this embodiment, the compound of formula (I) is:



(named Compound no. 3).

15 Still more preferably, the above-shown compound or the salt thereof is present as the free compound (e.g. as a substantially salt-free compound). For the purposes of the present patent application and invention, the above-shown compound, present as the free compound, is named Compound no. 3. This compound (as the enol ketone tautomer) was previously disclosed as compound A-66 in WO 2008/071405 A1, and can in general be synthesized using the methods of preparation disclosed in either WO 2008/071405 A1 or  
20 WO 2010/136431 A9.

In the compound of formula (I) or the salt thereof, in an alternative embodiment, R<sup>1</sup> is cyclopropyl and R<sup>2</sup> is chlorine. In this embodiment, the compound of formula (I) is:



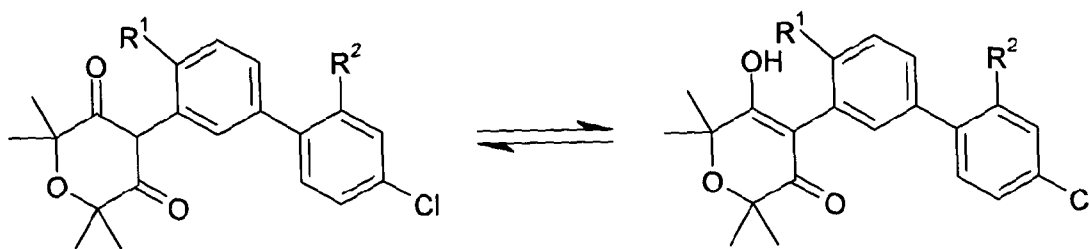
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(named Compound no. 4).

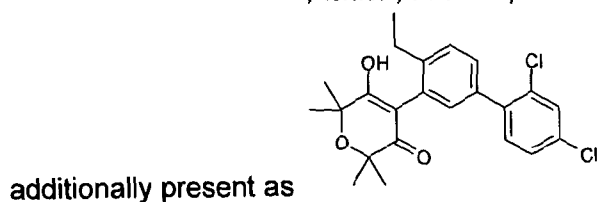
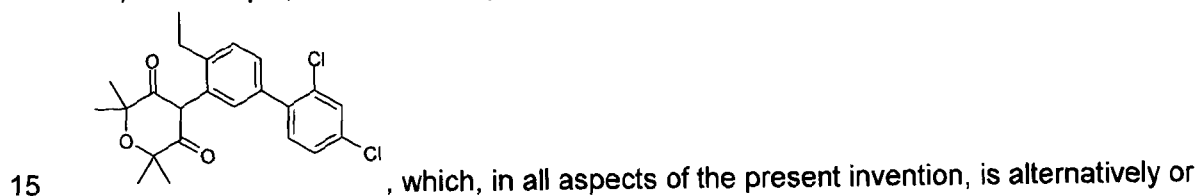
Still more preferably, the above-shown compound or the salt thereof is present as the free compound (e.g. as a substantially salt-free compound). For the purposes of the present

patent application and invention, the above-shown compound, present as the free compound, is named Compound no. 4. This compound (as the enol ketone tautomer) was previously disclosed as Example P9 within WO 2010/136431 A9, and can in general be synthesized using the methods of preparation disclosed in either WO 2008/071405 A1 or  
 5 WO 2010/136431 A9.

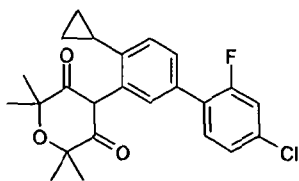
The compound of formula (I) can be present as the first or the second of the two equilibrating tautomeric forms shown below or as a mixture of both tautomeric forms. The compound of formula (I), as used in the present invention, encompasses the first tautomeric form, the  
 10 second tautomeric form, and a mixture of the first and second tautomeric forms:



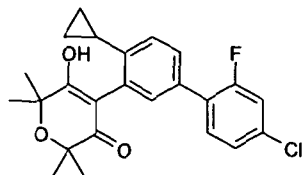
So, for example, when  $R^1$  is ethyl and  $R^2$  is chlorine, the compound of formula (I) is:



And, for example, when  $R^1$  is cyclopropyl and  $R^2$  is fluorine, the compound of formula (I) is:



, which, in all aspects of the present invention, is alternatively or

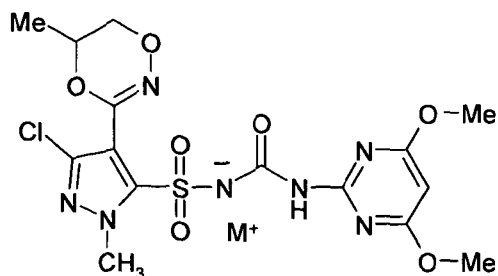


additionally present as

- 5 Preferred or particular or optional embodiments for the component (b), metazosulfuron or an agriculturally acceptable salt thereof, are as follows.

In one embodiment, an agriculturally acceptable salt of metazosulfuron is used, more particularly an agriculturally acceptable base addition salt such as an alkali metal (e.g.

- 10 sodium, potassium or lithium) salt thereof. An alkali metal (M) salt of metazosulfuron may, for example, have the following structure:



- 15 Preferably, however, the metazosulfuron or the salt thereof is present as the free compound (e.g. as a substantially salt-free compound).

Preferably, in general, the weight ratio of the compound of formula (I) or the salt thereof (e.g.

- 20 Compound no. 1 or 2, or a salt thereof), calculated as the free compound, to the metazosulfuron or the salt thereof, calculated as the free compound, is:

from 30:150 to 250:10 or from 30:120 to 250:15 or from 30:120 to 250:20, or more preferably from 50:120 to 180:20 (e.g. 60:100, 90:100, 120:100, 60:90, 90:90, 120:90, 60:60, 90:60, 120:60, 60:45, 90:45, 120:45, 60:22, 90:22 or 120:22) or from 50:120 to 150:35 (e.g. 60:100,

- 25 90:100, 120:100, 60:90, 90:90, 120:90, 60:60, 90:60, 120:60, 60:45, 90:45 or 120:45), or still



more preferably from 80:120 to 130:40 or from 80:110 to 130:40 (e.g. 90:100, 120:100, 90:90, 120:90, 90:60, 120:60, 90:45 or 120:45).

Preferably, for application (preferably foliar and/or spray application, e.g. post-emergence) to  
5 direct-seeded rice (e.g. dry-seeded rice or wet-sown rice; and/or preferably direct-seeded  
flooded rice), or for foliar and/or spray application (e.g. post-emergence) generally, the  
weight ratio of the compound of formula (I) or the salt thereof (e.g. Compound no. 1 or 2, or a  
salt thereof), calculated as the free compound, to the metazosulfuron or the salt thereof,  
calculated as the free compound, is:

10 from 30:100 to 150:10 or from 30:90 to 150:15 (e.g. 60:90, 90:90, 120:90, 60:60, 90:60,  
120:60, 60:45, 90:45, 120:45, 60:22, 90:22 or 120:22), or more preferably from 45:75 to  
130:15 or from 45:75 to 130:20, still more preferably from 60:60 to 120:20 (e.g. 60:60, 90:60,  
120:60, 60:45, 90:45, 120:45, 60:22, 90:22 or 120:22), yet more preferably from 60:50 to  
120:20 (e.g. 60:45, 90:45, 120:45, 60:22, 90:22 or 120:22), in particular from 60:50 to 90:20.

15

Preferably, for application to (preferably application to the flood-waters of) transplanted rice  
(preferably transplanted flooded rice), the weight ratio of the compound of formula (I) or the  
salt thereof (e.g. Compound no. 1 or 2, or a salt thereof), calculated as the free compound, to  
the metazosulfuron or the salt thereof, calculated as the free compound, is:

20 from 30:150 to 250:35 or from 30:120 to 250:35, or more preferably from 50:120 to 180:40 or  
from 50:120 to 150:40 (e.g. 60:100, 90:100, 120:100, 60:90, 90:90, 120:90, 60:60, 90:60,  
120:60, 60:45, 90:45 or 120:45), or still more preferably from 80:120 to 130:40 or from  
80:110 to 130:40 (e.g. 90:100, 120:100, 90:90, 120:90, 90:60, 120:60, 90:45 or 120:45).

25

The herbicidal compositions of the present invention can be prepared in a variety of ways  
using various formulation aids, such as carriers (e.g. liquid or solid carrier), solvents and/or  
surface-active substances. Therefore, preferably, the herbicidal composition of the present  
invention is a formulation comprising a carrier (e.g. liquid or solid carrier, preferably liquid), a  
30 solvent and/or a surface-active substance.

35

The herbicidal composition can be in various physical forms, for example in the form of a  
dustable powder (DP), a gel, a wettable powder (WP), a granule (GR) (such as an  
emulsifiable granule (EG) or more particularly a water-dispersible granule (WG)), a water-  
dispersible tablet (WT), an effervescent compressed tablet, an emulsifiable concentrate (EC),  
a microemulsifiable concentrate, an oil-in-water emulsion (EW), an oil flowable (e.g. a

spreading oil (SO)), an aqueous dispersion (e.g. aqueous suspension concentrate (SC)), an oily dispersion (OD), a suspo-emulsion (SE), a capsule suspension (CS), a soluble liquid, a water-soluble concentrate (with water or a water-miscible organic solvent as carrier), an impregnated polymer film, or in another form such as a form known, for example, from the  
5 Manual on Development and Use of FAO Specifications for Plant Protection Products, 5th Edition, 1999.

Preferably, the herbicidal composition is in the form of a wettable powder (WP), a granule (GR) (such as an emulsifiable granule (EG) or more particularly a water-dispersible granule  
10 (WG)), an emulsifiable concentrate (EC), a microemulsifiable concentrate, an oil-in-water emulsion (EW), an oil flowable (e.g. a spreading oil (SO)), an aqueous dispersion (e.g. aqueous suspension concentrate (SC)), an oily dispersion (OD), a soluble liquid, or a water-soluble concentrate (wherein the water-soluble concentrate is with water or a water-miscible organic solvent as carrier).

15 More preferably, the herbicidal composition is in the form of an emulsifiable concentrate (EC).

The herbicidal composition of the invention can for example be used directly or, more  
20 typically, can be diluted prior to use. Diluted liquid herbicidal compositions can be prepared, for example, by mixing (e.g. in a tank) the herbicidal composition of the invention with water, fertiliser(s) (e.g. liquid or granular fertiliser(s)), micronutrient(s), biological organism(s), oil and/or solvent(s); and/or by mixing the herbicidal composition of the invention with water and optionally other ingredients (typically fertiliser(s), micronutrient(s), biological organism(s), oil  
25 and/or solvent(s)).

The herbicidal compositions can be prepared, for example, by mixing the active ingredient with one or more formulation aids. The composition can e.g. be formed in the form of finely divided solids, granules, solutions, dispersions or emulsions. The active ingredients can also  
30 be mixed with other formulation aids, for example finely divided solids, mineral oils, vegetable oils, modified vegetable oils, organic solvents, water, surface-active substances or combinations thereof. The active ingredients can also be contained in very fine microcapsules consisting of a polymer. Microcapsules contain the active ingredients in a porous carrier. This enables the active ingredients to be released into their surroundings in  
35 controlled amounts (e.g. slow release). Microcapsules usually have a diameter of from 0.1 to 500 microns. They contain active ingredients in an amount of about from 25 to 95 % by

weight of the capsule weight. The active ingredients can be present in the form of a monolithic solid, in the form of fine particles in solid or liquid dispersion or in the form of a suitable solution. The encapsulating membranes comprise, for example, natural and synthetic gums, cellulose, styrene-butadiene copolymers, polyacrylonitrile, polyacrylate, polyester, polyamides, polyureas, polyurethane or chemically modified polymers and starch xanthates or other polymers that are known to the person skilled in the art in this connection. Alternatively it is possible for very fine microcapsules to be formed wherein the active ingredient is present in the form of finely divided particles in a solid matrix of a base substance, but in that case the microcapsule is not encapsulated.

10

The formulation aids suitable for the preparation of the compositions according to the invention can include those known *per se*.

As liquid carrier (and/or solvent) there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylenes carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid (e.g. ethyl acetate, butyl acetate, amyl acetate, or isoamyl acetate, et al.), diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, N,N-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethyl-hexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxypropanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, n-hexane, n-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol (PEG 400), propionic acid, propyl lactate, propylene carbonate, propylene glycol, propylene glycol methyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylenesulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol methyl ether, diethylene glycol methyl ether, methanol, ethanol, isopropanol, or higher molecular weight alcohols (i.e. an alcohol having a higher molecular weight than isopropanol, such as amyl alcohol, tetrahydrofurfuryl alcohol,

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hexanol, octanol, 2-ethyl-hexanol, cyclohexanol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, hexylene glycol, or glycerol), or *N*-methyl-2-pyrrolidone, *N*-octyl-2-pyrrolidone, a mixture of heavy aromatic hydrocarbons (e.g. containing a mixture of C<sub>1</sub>-C<sub>4</sub>alkylnaphthalenes and optionally also naphthalene, e.g. Solvesso 200™) or a similar liquid carrier (and/or a similar solvent).

Water is generally the carrier of choice for the dilution of a concentrate (e.g. emulsifiable concentrate) herbicidal composition.

Suitable solid carriers are, for example, talc, titanium dioxide, pyrophyllite clay, silica (silicon dioxide), attapulgite clay, kieselguhr, limestone, calcium carbonate, bentonite, calcium montomorillonite, cottonseed husks, wheatmeal, soybean flour, pumice, wood flour, ground walnut shells, lignin and/or similar materials, as described, for example, in CFR 180.1001. (c) & (d).

15

A surface-active substance can advantageously be used both in solid and in liquid herbicidal compositions, especially in those herbicidal compositions which can be diluted with a carrier prior to use. Surface-active substances may be anionic, cationic, non-ionic or polymeric and they may be used as emulsifying, wetting or suspending agents or for other purposes.

Typical surface-active substances include, for example, salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; salts of alkylarylsulfonates, such as calcium dodecylbenzenesulfonate; alkylphenol-alkylene oxide addition products, such as nonylphenol ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol ethoxylate; soaps, such as sodium stearate; salts of alkylnaphthalenesulfonates, such as sodium dibutylnaphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryl trimethylammonium chloride, polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; and salts of mono- and di-alkyl phosphate esters; and also further substances described e.g. in "McCutcheon's Detergents and Emulsifiers Annual", MC Publishing Corp., Ridgewood, New Jersey, 1981.

Further formulation aids which can usually be used in the herbicidal composition include crystallisation inhibitors, viscosity-modifying substances, suspending agents, dyes, anti-oxidants, foaming agents, light absorbers, mixing aids, anti-foams, complexing agents, neutralising or pH-modifying substances and/or buffers, corrosion-inhibitors, fragrances,

35

wetting agents, absorption improvers, micronutrients, plasticisers, glidants, lubricants, dispersants, thickeners, anti-freezes, microbiocides, and/or liquid and/or solid fertilisers.

The herbicidal compositions may also comprise additional active substances, for example  
5 one or more further herbicides, herbicide safeners, plant growth regulators, fungicides and/or insecticides.

The compositions according to the invention can additionally include an additive comprising  
10 an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive used in the composition according to the invention is generally from 0.01 to 10 %, based on the spray mixture. For example, the oil additive can be added to the spray tank in the desired concentration after the spray mixture has been prepared. Preferred oil additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, emulsified vegetable oil, such as AMIGO®  
15 (Rhône-Poulenc Canada Inc.), alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow. A preferred additive contains, for example, as active components essentially 80 % by weight alkyl esters of fish oils and 15 % by weight methylated rapeseed oil, and also 5 % by weight of customary emulsifiers and pH modifiers. Especially preferred oil additives comprise alkyl esters of  
20 C<sub>8</sub>-C<sub>22</sub> fatty acids, especially the methyl derivatives of C<sub>12</sub>-C<sub>18</sub> fatty acids, for example the methyl esters of lauric acid, palmitic acid and oleic acid, being important. Those esters are known as methyl laurate (CAS-111-82-0), methyl palmitate (CAS-112-39-0) and methyl oleate (CAS-112-62-9). A preferred fatty acid methyl ester derivative is Emery® 2230 and 2231 (Cognis GmbH). Those and other oil derivatives are also known from the Compendium  
25 of Herbicide Adjuvants, 5th Edition, Southern Illinois University, 2000.

The application and action of the oil additives can be further improved by combining them with surface-active substances, such as non-ionic, anionic or cationic surfactants. Examples of suitable anionic, non-ionic and cationic surfactants are listed on pages 7 and 8 of  
30 WO 97/34485. Preferred surface-active substances are anionic surfactants of the dodecyl-benzylsulfonate type, especially the calcium salts thereof, and also non-ionic surfactants of the fatty alcohol ethoxylate type. Special preference is given to ethoxylated C<sub>12</sub>-C<sub>22</sub> fatty alcohols having a degree of ethoxylation of from 5 to 40. Examples of commercially available surfactants are the Genapol types (Clariant AG). Also preferred are silicone surfactants,  
35 especially polyalkyl-oxide-modified heptamethyltrisiloxanes, which are commercially available e.g. as Silwet L-77®, and also perfluorinated surfactants. The concentration of

surface-active substances in relation to the total additive is generally from 1 to 30 % by weight. Examples of oil additives that comprise or consist of mixtures of oils or mineral oils or derivatives thereof with surfactants are Edenor ME SU<sup>®</sup>, Turbocharge<sup>®</sup> (a mixture of surfactant, 1-octanol and petroleum oil) (Syngenta AG, CH), and Actipron<sup>®</sup> (BP Oil UK  
5 Limited, GB).

The said surface-active substances may also be used in the herbicidal compositions alone, that is to say without oil additives.

10 Furthermore, the addition of an organic solvent to the oil additive/surfactant mixture can contribute to a further enhancement of action. Suitable solvents are, for example, Solvesso<sup>®</sup> (ESSO) and Aromatic Solvent<sup>®</sup> (Exxon Corporation). The concentration of such solvents can be from 10 to 80 % by weight of the total weight. Such oil additives, which may be in admixture with solvents, are described, for example, in US-A-4 834 908. A commercially  
15 available oil additive disclosed therein is known by the name MERGE<sup>®</sup> (BASF Corporation). A further oil additive that is preferred according to the invention is SCORE<sup>®</sup> (Syngenta Crop Protection Canada.)

In addition to the oil additives listed above, in order to enhance the activity of the compositions according to the invention it is also possible for compositions of alkylpyrrolidones, (e.g. Agrimax<sup>®</sup>) to be added to the spray mixture. Compositions of synthetic latices, such as, for example, polyacrylamide, polyvinyl compounds or poly-1-p-menthene (e.g. Bond<sup>®</sup>, Courier<sup>®</sup> or Emerald<sup>®</sup>) can also be used. Solutions that contain propionic acid, for example Eurogkem Pen-e-trate<sup>®</sup>, can also be mixed into the spray mixture as activity-enhancing agents.  
20

25

The herbicidal compositions generally contain:

- (a) from 0.1 to 99 % by weight, especially from 0.5 to 95 % by weight, more especially from 1 to 60 % by weight or from 1 to 40 % by weight, of the compound of formula (I) or the salt thereof; and  
30 (b) from 0.1 to 99 % by weight, especially from 0.5 to 95 % by weight, more especially from 1 to 60 % by weight or from 1 to 40 % by weight, of the metazosulfuron or the salt thereof; and  
(b) from 5 to 99.5%, or from 20 to 98%, or from 40% to 95%, by weight) of one or more formulation aids (e.g. a total of from 5 to 99.5%, or from 20 to 98%, or from 40% to 95%, by weight of the herbicidal composition, of: any carrier (e.g. liquid or solid carrier) (if present),  
35 any solvent (if present), any surface-active substance (if present), and any other formulation aids which may be present).

The formulation aid(s) preferably include(s) from 1 to 25 % by weight of a surface-active substance, e.g. one or more emulsifiers.

- 5 Unless the context requires otherwise, in this specification, % by weight means % by weight of the herbicidal composition.

Whereas commercial products (e.g. liquid herbicidal compositions) will preferably be formulated as concentrates, the end user will normally employ diluted formulations.

10

Preferred formulations have especially the following compositions:  
(% = percent by weight of the herbicidal composition or formulation):

Emulsifiable concentrates:

- 15 active ingredient: 1 to 95 %, in particular 1 to 60 % (e.g. 1 to 40 %) or 60 to 90 %  
 surface-active agent: 1 to 30 %, preferably 5 to 30 % or 5 to 20 %  
 liquid carrier (and/or solvent): 1 to 90 % or 1 to 80 %, in particular 1 to 35 % or 35 to 90 % (such as 35 to 80 %)

20

Dusts:

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

25 Suspension concentrates:

- active ingredient: 2 to 75 % or 5 to 75 %, preferably 10 to 50 %  
 water: 94 to 24 %, preferably 88 to 30 %  
 surface-active agent: 1 to 40 %, preferably 2 to 30 %

30 Wettable powders:

- active ingredient: 0.5 to 90 %, preferably 1 to 80 %  
 surface-active agent: 0.5 to 20 %, preferably 1 to 15 %  
 solid carrier: 5 to 95 %, preferably 15 to 90 %

35 Granules:

- active ingredient: 0.1 to 30 %, preferably 0.1 to 15 %

solid carrier: 99.5 to 70 %, preferably 97 to 85 %,

where the term "active ingredient" refers to the mixture of compound of formula (I) with a co-herbicide.

5

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

<u>F1. Emulsifiable concentrates</u>		a)	b)	c)	d)
	active ingredient	5 %	10 %	25 %	50 %
10	calcium dodecylbenzene-sulfonate	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 %
15	NMP ( <i>N</i> -methylpyrrolidone)	-	-	10 %	20 %
	aromatic hydrocarbon mixture C <sub>9</sub> -C <sub>12</sub>	85 %	78 %	55 %	16 %

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

20

<u>F2. Solutions</u>		a)	b)	c)	d)
	active ingredient	5 %	10 %	50 %	90 %
25	1-methoxy-3-(3-methoxy-propoxy)-propane	-	20 %	20 %	-
	polyethylene glycol MW 400	20 %	10 %	-	-
	NMP ( <i>N</i> -methylpyrrolidone)	-	-	30 %	10 %
	aromatic hydrocarbon mixture C <sub>9</sub> -C <sub>12</sub>	75 %	60 %	-	-

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

30

<u>F3. Wettable powders</u>		a)	b)	c)	d)
	active ingredient	5 %	25 %	50 %	80 %
	sodium lignosulfonate	4 %	-	3 %	-
35	sodium lauryl sulfate	2 %	3 %	-	4 %
	sodium diisobutyl-naphthalene-				



- 16 -

	sulfonate	-	6 %	5 %	6 %
	octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	1 %	2 %	-
	highly dispersed silicic acid	1 %	3 %	5 %	10 %
5	kaolin	88 %	62 %	35 %	-

The active ingredient is thoroughly mixed with the formulation aid(s) and the mixture is thoroughly ground in a suitable mill, yielding wettable powders which can be diluted with water to give suspensions of any desired concentration.

10	<u>F4. Coated granules</u>	a)	b)	c)
	active ingredient	0.1 %	5 %	15 %
	highly dispersed silicic acid	0.9 %	2 %	2 %
	inorganic carrier (diameter 0.1 - 1 mm)	99.0 %	93 %	83 %

15 e.g. CaCO<sub>3</sub> or SiO<sub>2</sub>

The active ingredient is dissolved in methylene chloride, the solution is sprayed onto the carrier and the solvent is subsequently evaporated off *in vacuo*.

	<u>F5. Coated granules</u>	a)	b)	c)
20	active ingredient	0.1 %	5 %	15 %
	polyethylene glycol MW 200	1.0 %	2 %	3 %
	highly dispersed silicic acid	0.9 %	1 %	2 %
	inorganic carrier (diameter 0.1 - 1 mm)	98.0 %	92 %	80 %

25 e.g. CaCO<sub>3</sub> or SiO<sub>2</sub>

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

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

35 The active ingredient is mixed and ground with the formulation aid(s) and the mixture is moistened with water. The resulting mixture is extruded and then dried in a stream of air.

- 17 -

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

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

<u>F8. Suspension concentrates</u>	a)	b)	c)	d)
active ingredient	3 %	10 %	25 %	50 %
10 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 %
15 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 %

20 The finely ground active ingredient is intimately mixed with the formulation aid(s), yielding a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

25 The term "active ingredient" in the examples mentioned above refers to the mixture of compound of formula (I) with a co-herbicide.

30 A **second aspect** of the present invention relates to a method of controlling weeds in crops of useful plants, which comprises applying a herbicidal composition of the invention as defined herein to the weeds and/or useful plants (e.g. flooded weeds and/or flooded useful plants) and/or to the locus (e.g. flooded locus) thereof.

35 The second aspect of the invention also relates also to a method for the control (e.g. selective control) of weeds in crops of useful plants, which comprises treating the weeds and/or useful plants (e.g. flooded weeds and/or flooded useful plants), and/or the area under

cultivation (e.g. flooded area), and/or the locus (e.g. flooded locus) thereof, with a herbicidal composition according to this invention.

5 The invention also relates to a herbicidal composition as defined herein, for controlling weeds in crops of useful plants (e.g. flooded plants), especially in crops of rice (e.g. flooded rice).

In all aspects of the invention, the application of the herbicidal composition is preferably post-emergence (e.g. after the emergence of the crop(s) and/or the weed(s)).

10 The crops of useful plants, e.g. in which the compositions according to the invention can be used, are in particular cereals, cotton, soybeans, sugar beet, sugar cane, potatoes, plantation crops, rape (e.g. oilseed rape), maize or rice; or more particularly cotton, soybeans, sugar beet, sugar cane, potatoes, rape (e.g. oilseed rape), or rice.

15 The crops of useful plants are preferably rice, in particular indica rice (such as IR-64, Ciherang, Pusa e.g. Pusa-1121, Jiayu 293, or NK-3325 hybrid); or japonica rice (such as Koshihikari, Arborio, or Liangyou peiju e.g. Liangyou peiju PS3100).

The rice is preferably flooded rice.

20

The rice can for example be direct-seeded [e.g. dry-sown (dry-seeded) or wet-sown] rice; which can optionally be flooded (e.g. before or after the herbicidal composition is applied). However, preferably the rice is transplanted rice, which is typically flooded (e.g. before the herbicidal composition is applied).

25

Non-selective weed control might also be a possibility in some circumstances.

30 The weeds to be controlled may be monocotyledonous and/or dicotyledonous weeds, such as, for example, *Echinochloa* (e.g. *Echinochloa crus-galli*), *Brachiaria* (e.g. *Brachiaria plantaginina*), *Leptochloa* (e.g. *Leptochloa chinensis*), *Digitaria*, *Setaria*, *Scirpus* (e.g. *Scirpus maritimus* or *Scirpus juncooides*), *Monochoria*, *Fimbristylis*, *Cyperus*, *Commelina*, *Sagittaria*, *Elatine*, *Lindernia*, *Ludwigia*, *Stellaria*, *Nasturtium*, *Agrostis*, *Avena*, *Sinapis*, *Lolium*, *Solanum*, *Bromus*, *Alopecurus*, *Sorghum*, *Rottboellia*, *Abutilon*, *Sida*, *Xanthium*, *Amaranthus*, *Chenopodium*, *Ipomoea*, *Chrysanthemum*, *Galium*, *Viola*, *Veronica*, and/or *Schoenoplectus*.

35

Preferably, the weeds to be controlled comprise: monocotyledonous weeds, and/or weeds found in rice fields e.g. rice paddy fields. Preferably, the weeds to be controlled comprise: *Echinochloa* (e.g. *Echinochloa crus-galli* (ECHCG), *Echinochloa oryzoides*, *Echinochloa colona* or *colonom* (ECHCO), *Echinochloa crus-pavonis*, or *Echinochloa oryzicola*; or  
5 *Echinochloa muricata* or *Echinochloa stagnina*), *Brachiaria* (e.g. *Brachiaria plantaginina* (BRAPL)), *Leptochloa* (e.g. *Leptochloa chinensis* (LEFCH) or *Leptochloa panicoides*), *Digitaria*, *Setaria*, *Scirpus* (e.g. *Scirpus maritimus* (SCPMA), *Scirpus juncoides* (SCPJU), *Scirpus maritimus*, *Scirpus fluviatilis*, *Scirpus pendulus*, *Scirpus triangulatus*, or one of many other *Scirpus* species), *Monochoria* (e.g. *Monochoria vaginalis* (MOOVA) or *Monochoria*  
10 *korsakovii*), *Fimbristylis* (e.g. *Fimbristylis miliacea* (FIMMI)), *Cyperus* (e.g. *Cyperus serotinus*), *Commelina*, *Sagittaria*, *Elatine*, *Lindernia* and/or *Ludwigia*; and/or *Schoenoplectus* (e.g. *Schoenoplectus mucronatus* or *Schoenoplectus juncoides*).

More preferably, the weeds to be controlled comprise: *Echinochloa* (e.g. *Echinochloa crus-galli* (ECHCG), *Echinochloa oryzoides*, *Echinochloa colona* or *colonom* (ECHCO),  
15 *Echinochloa crus-pavonis*, or *Echinochloa oryzicola*; or *Echinochloa muricata* or *Echinochloa stagnina*), *Brachiaria* (e.g. *Brachiaria plantaginina* (BRAPL)), *Leptochloa* (e.g. *Leptochloa chinensis* (LEFCH) or *Leptochloa panicoides*), *Scirpus* (e.g. *Scirpus maritimus* (SCPMA), *Scirpus juncoides* (SCPJU), *Scirpus maritimus*, *Scirpus fluviatilis*, *Scirpus pendulus*, *Scirpus*  
20 *triangulatus*, or one of many other *Scirpus* species), *Monochoria* (e.g. *Monochoria vaginalis* (MOOVA) or *Monochoria korsakovii*), *Fimbristylis* (e.g. *Fimbristylis miliacea* (FIMMI)), and/or *Cyperus* (e.g. *Cyperus serotinus*).

Most preferably, the weeds to be controlled comprise *Echinochloa*, such as *Echinochloa*  
25 *crus-galli* (ECHCG), and/or *Brachiaria*, such as *Brachiaria plantaginina* (BRAPL).

Still more preferably, the weeds to be controlled (e.g. comprising *Echinochloa*) are in crops of flooded rice, especially crops of flooded transplanted rice.

30 The term "crops" is to be understood as also including crops that have been rendered tolerant to herbicides or classes of herbicides (for example ALS, GS, EPSPS, PPO, ACCase or HPPD inhibitors) as a result of conventional methods of breeding or genetic engineering. Examples of crop that have been rendered tolerant e.g. to imidazolinones, such as imazamox, by conventional methods of breeding are Clearfield® summer rape (Canola) or  
35 Clearfield® rice. Examples of crops that have been rendered tolerant to herbicides by genetic engineering methods include e.g. glyphosate-resistant or glufosinate-resistant maize

or rice varieties, e.g. those commercially available under the trade names RoundupReady® (glyphosate-resistant maize or rice) or LibertyLink® (glufosinate-resistant maize or rice).

5 Crops are also to be understood as being those which have been rendered resistant to harmful insects by genetic engineering methods, for example Bt maize (resistant to European corn borer), Bt cotton (resistant to cotton boll weevil) and also Bt potatoes (resistant to Colorado beetle). Examples of Bt maize are the Bt-176 maize hybrids of NK® (Syngenta Seeds). The Bt toxin is a protein that is formed naturally by *Bacillus thuringiensis* soil bacteria. Examples of toxins and transgenic plants able to synthesise such toxins are described in EP-A-451 878, EP-A-374 753, WO 93/07278, WO 95/34656, WO 03/052073 and EP-A-427 529. Examples of transgenic plants that contain one or more genes which code for an insecticidal resistance and express one or more toxins are KnockOut® (maize), Yield Gard® (maize), NuCOTIN33B® (cotton), Bollgard® (cotton), NewLeaf® (potatoes), NatureGard® and Protexcta®. Plant crops and their seed material can be resistant to herbicides and at the same time also to insect feeding ("stacked" transgenic events). Seed can, for example, have the ability to express an insecticidally active Cry3 protein and at the same time be glyphosate-tolerant. The term "crops" is to be understood as also including crops obtained as a result of conventional methods of breeding or genetic engineering which contain so-called output traits (e.g. improved flavour, storage stability, nutritional content).

20 Areas under cultivation are to be understood as including land where the crop plants are already growing as well as land intended for the cultivation of those crop plants.

25 The rates of application of each of the herbicides (the compound of formula (I) or salt, and separately the metazosulfuron or salt) may vary within wide limits, and for example can depend upon 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/or other factors governed by the method of application, the time of application and/or the target crop.

30 In the method of controlling (or for the control of) weeds in crops of useful plants (e.g. rice) and/or in the herbicidal composition for controlling weeds in crops of useful plants (e.g. rice), according to the invention, and/or in other aspects of the invention, preferably, the herbicidal composition is applied to the plants and/or the weeds, or to the locus thereof, at an application rate as defined below.

35

Preferably, in general, the application rate for the compound of formula (I) or the salt thereof (e.g. Compound no. 1 or 2, or a salt thereof), is:

from 30 to 250 g/ha, e.g. 60, 90, 120 or 240 g/ha; preferably from 50 to 180 g/ha or from 50 to 150 g/ha, e.g. 60, 90 or 120 g/ha; more preferably from 80 to 130 g/ha or from 90 to 120 g/ha, e.g. 90 or 120 g/ha;

5

of the compound of formula (I) or a salt thereof (e.g. Compound no. 1 or 2, or a salt thereof), calculated as the free compound. "ha" = hectare.

Preferably, in general, the application rate for the metazosulfuron or the salt thereof is:

10 from 10 to 150 g/ha or from 15 to 140 g/ha or from 20 to 120 g/ha, e.g. 22, 45, 60, 90 or 100 g/ha; more preferably from 35 to 120 g/ha or from 40 to 110 g/ha, e.g. 45, 60, 90 or 100 g/ha; of the metazosulfuron or the salt thereof, calculated as the free compound.

Preferably, for application (preferably foliar and/or spray application) to direct-seeded rice

15 (e.g. dry-seeded rice or wet-sown rice; and/or preferably direct-seeded flooded rice), the application rate for the compound of formula (I) or the salt thereof (e.g. Compound no. 1 or 2, or a salt thereof), is:

from 30 to 150 g/ha, more preferably from 30 to 130 g/ha, still more preferably from 45 to 130 g/ha, yet more preferably from 60 to 120 g/ha (e.g. 60, 90 or 120 g/ha), such as from from 60 to 90 g/ha;

20

of the compound of formula (I) or a salt thereof (e.g. Compound no. 1 or 2, or a salt thereof), calculated as the free compound. "ha" = hectare.

Preferably, for application (preferably foliar and/or spray application) to direct-seeded rice

25 (e.g. dry-seeded rice or wet-sown rice; and/or preferably direct-seeded flooded rice), the application rate for the metazosulfuron or the salt thereof is:

from 10 to 100 g/ha (e.g. 22, 45, 60, 90 or 100 g/ha) or from 15 to 90 g/ha; more preferably from 15 to 75 g/ha or from 20 to 75 g/ha, e.g. 22, 45 or 60 g/ha; still more preferably from 20 to 60 g/ha, e.g. 22, 45 or 60 g/ha, yet more preferably from 20 to 50 g/ha, e.g. 22 or 45 g/ha;

30

of the metazosulfuron or the salt thereof, calculated as the free compound.

Preferably, for application to (preferably application to the flood-waters of) transplanted rice (preferably transplanted flooded rice), the application rate for the compound of formula (I) or the salt thereof (e.g. Compound no. 1 or 2, or a salt thereof), is:

from 30 to 250 g/ha, e.g. 60, 90, 120 or 240 g/ha; preferably from 50 to 180 g/ha or from 50 to 150 g/ha, e.g. 60, 90 or 120 g/ha; more preferably from 80 to 130 g/ha or from 90 to 120 g/ha, e.g. 90 or 120 g/ha;

of the compound of formula (I) or a salt thereof (e.g. Compound no. 1 or 2, or a salt thereof),  
5 calculated as the free compound. "ha" = hectare.

Preferably, for application to (preferably application to the flood-waters of) transplanted rice (preferably transplanted flooded rice), the application rate for the metazosulfuron or the salt thereof is:

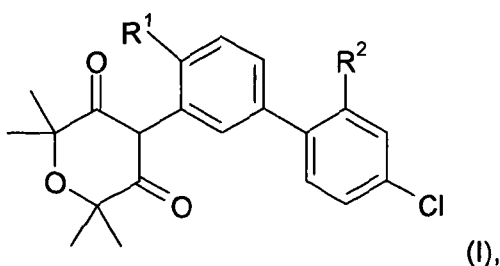
10 from 35 to 150 g/ha or from 35 to 140 g/ha or from 35 to 120 g/ha, e.g. 45, 60, 90 or 100 g/ha; more preferably from 40 to 120 g/ha, e.g. 45, 60, 90 or 100 g/ha; still more preferably from 50 to 120 g/ha or from 60 to 110 g/ha, e.g. 60, 90 or 100 g/ha, most preferably from 80 to 110 g/ha, e.g. 90 or 100 g/ha;

of the metazosulfuron or the salt thereof, calculated as the free compound.

15

A **third aspect** of the present invention provides a herbicidal composition comprising:

(a) a compound of formula (I) or an agriculturally acceptable salt thereof:



20

wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine;  
and

(b) halosulfuron-methyl or an agriculturally acceptable salt thereof,

wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the  
25 free compound, to the halosulfuron-methyl or the salt thereof, calculated as the free compound, is from 30:60 to 250:3.

Preferred features of this third aspect of the invention are generally as described herein for the first and other aspects of the invention. For example, preferably, in the compound of  
30 formula (I) or the salt thereof, R<sup>1</sup> is ethyl and R<sup>2</sup> is chlorine, or R<sup>1</sup> is cyclopropyl and R<sup>2</sup> is fluorine.

In one embodiment, an agriculturally acceptable salt of halosulfuron-methyl is used, more particularly an agriculturally acceptable base addition salt such as an alkali metal (e.g. sodium, potassium or lithium) salt thereof.

- 5 Preferably, however, the halosulfuron-methyl or the salt thereof is present as the free compound (e.g. as a substantially salt-free compound).

Preferably, in general, the weight ratio of the compound of formula (I) or the salt thereof (e.g. Compound no. 1 or 2, or a salt thereof), calculated as the free compound, to the  
10 halosulfuron-methyl or the salt thereof, calculated as the free compound, is:  
from 30:40 to 250:5 or from 50:60 to 180:3, or more preferably from 50:40 to 180:5 or from 50:40 to 150:5, or still more preferably from 50:30 to 180:5 from 50:30 to 150:5 or from 50:20 to 150:10 (e.g. 60:20, 90:20, 120:20, 60:15, 90:15, 120:15, 60:10, 90:10 or 120:10).

- 15 A **fourth aspect** of the present invention relates to a method of controlling weeds in crops of useful plants, which comprises applying a herbicidal composition as defined in the third aspect of the invention to the weeds and/or useful plants (e.g. flooded weeds and/or flooded useful plants) and/or to the locus (e.g. flooded locus) thereof.
- 20 The preferable features of the fourth aspect of the invention are generally as described herein for the second aspect of the invention.

Preferably, in general, the application rate for the halosulfuron-methyl or the salt thereof is:  
from 3 to 60 g/ha, more preferably from 5 to 40 g/ha or from 5 to 30 g/ha, still more  
25 preferably from 10 to 20 g/ha, e.g. 10, 15 or 20 g/ha;  
of the halosulfuron-methyl or the salt thereof, calculated as the free compound.

A **fifth aspect** of the invention provides a method of controlling *Brachiaria* weeds (e.g.  
30 *Brachiaria plantaginina* (BRAPL)), and/or e.g. flooded *Brachiaria* weeds) in crops of useful plants (e.g. cotton, soybeans, sugar beet, sugar cane, potatoes, or rape (e.g. oilseed rape), or most preferably rice, e.g. flooded and/or transplanted rice), which comprises applying a compound of formula (I) or an agriculturally acceptable salt thereof (preferably Compound no. 1 or 2, or a salt thereof), to the *Brachiaria* weeds or to the locus (e.g. flooded locus)  
35 thereof; preferably post-emergence. In this method, preferably, the compound of formula (I) or the salt thereof is applied at an application rate of:



- 24 -

from 30 to 250 g/ha, e.g. 60, 90, 120 or 240 g/ha; preferably from 50 to 180 g/ha or from 50 to 150 g/ha, e.g. 60, 90 or 120 g/ha; more preferably from 80 to 130 g/ha or from 90 to 120 g/ha, e.g. 90 or 120 g/ha;

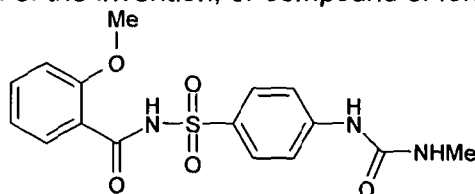
of the compound of formula (I) or the salt thereof (preferably Compound no. 1 or 2, or a salt thereof), calculated as the free compound. "ha" = hectare.

Preferably, in this fifth aspect of the invention, the compound of formula (I) or the salt thereof is not applied to the *Brachiaria* weeds or to the locus thereof together with (e.g. in a herbicidal composition containing) any of: fenoxasulfone, ipfencarbazone, propyrisulfuron, or *N*-[2-[(4,6-dimethoxy-1,3,5-triazin-2-yl)carbonyl]-6-fluorophenyl]-1,1-difluoro-*N*-methylmethanesulfonamide, or a salt of any of these.

Compound no. 1 or 2 alone appear to be herbicidally active (ca. 75-98%) against *Brachiaria plantaginia*, with little (0% to 5%) phytotoxicity on IR-64 indica rice, when applied by post-emergent foliar spray application as an EC formulation at an application rate of 90 or 120 g/ha of Compound no. 1 or at an application rate of 60, 90 or 120 g/ha of Compound no. 2 (see Biological Example 1 herein).

In all aspects of the invention, the herbicidal composition (and/or compound of formula (I) or salt thereof) according to any aspect of the invention described herein (above or below) can also be used in combination with one or more safeners. The following mixtures with safeners, especially, come into consideration:

[herbicidal composition of the invention, or compound of formula (I) or salt] + a compound of



the following formula:

(e.g. as disclosed in EP 0 365

484 A – see e.g. compound 1.028 therein – or e.g. as disclosed in WO 2009/056333 or WO 2011/064533),

[herbicidal composition of the invention, or compound of formula (I) or salt] + cyprosulfamide,  
[herbicidal composition of the invention, or compound of formula (I) or salt] + cloquintocet-mexyl,

[herbicidal composition of the invention, or compound of formula (I) or salt] + cloquintocet acid or a salt thereof,

[herbicidal composition of the invention, or compound of formula (I) or salt] + fenchlorazole-ethyl,

[herbicidal composition of the invention, or compound of formula (I) or salt] + fenchlorazole acid or a salt thereof,

5 [herbicidal composition of the invention, or compound of formula (I) or salt] + mefenpyr-diethyl,

[herbicidal composition of the invention, or compound of formula (I) or salt] + mefenpyr diacid,

[herbicidal composition of the invention, or compound of formula (I) or salt] + isoxadifen-ethyl,

10 [herbicidal composition of the invention, or compound of formula (I) or salt] + isoxadifen acid,

[herbicidal composition of the invention, or compound of formula (I) or salt] + furilazole,

[herbicidal composition of the invention, or compound of formula (I) or salt] + furilazole *R*-isomer,

[herbicidal composition of the invention, or compound of formula (I) or salt] + benoxacor,

15 [herbicidal composition of the invention, or compound of formula (I) or salt] + dichlormid,

[herbicidal composition of the invention, or compound of formula (I) or salt] + AD-67,

[herbicidal composition of the invention, or compound of formula (I) or salt] + oxabetrinil,

[herbicidal composition of the invention, or compound of formula (I) or salt] + cyometrinil,

20 [herbicidal composition of the invention, or compound of formula (I) or salt] + cyometrinil *Z*-isomer,

[herbicidal composition of the invention, or compound of formula (I) or salt] + fenclorim,

[herbicidal composition of the invention, or compound of formula (I) or salt] + naphthalic anhydride,

[herbicidal composition of the invention, or compound of formula (I) or salt] + flurazole,

25 [herbicidal composition of the invention, or compound of formula (I) or salt] + CL 304,415,

[herbicidal composition of the invention, or compound of formula (I) or salt] + dicyclonon,

[herbicidal composition of the invention, or compound of formula (I) or salt] + fluxofenim,

[herbicidal composition of the invention, or compound of formula (I) or salt] + DKA-24,

[herbicidal composition of the invention, or compound of formula (I) or salt] + R-29148, or

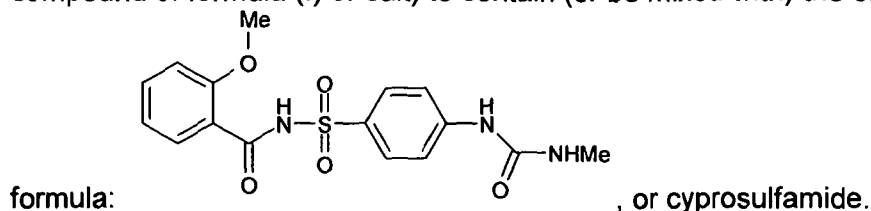
30 [herbicidal composition of the invention, or compound of formula (I) or salt] + PPG-1292.

The above-mentioned safeners are described, for example, in the Pesticide Manual, Twelfth Edition, British Crop Protection Council, 2000. R-29148 is described, for example by P.B. Goldsbrough et al., Plant Physiology, (2002), Vol. 130 pp. 1497-1505 and references therein;

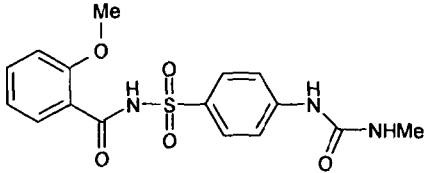
35 and PPG-1292 is known from WO 2009/211761.

A safening effect is also thought to be possible for the mixtures of the compound of the formula (I) + dymron.

As a preferable safener, it is preferable for the herbicidal composition of the invention (or the compound of formula (I) or salt) to contain (or be mixed with) the compound of the following

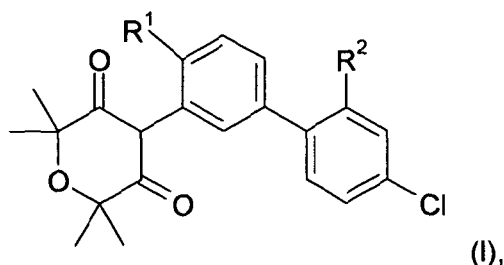


Preferably, the weight ratio of the compound of formula (I) or salt thereof (e.g. Compound no. 1 or 2, or salt thereof), calculated as the free compound, to the safener (e.g. the compound

10 of formula  , or cyprosulfamide) is from 20:1 to 1:2, more preferably from 8:1 to 1:2 (e.g. 8:1, 4:1 or 2:1), still more preferably from 4:1 to 1:1, e.g. 4:1 or 2:1.

According to a further aspect of the invention there is provided a herbicidal composition comprising:

15 (a) a compound of formula (I) or an agriculturally acceptable salt thereof:



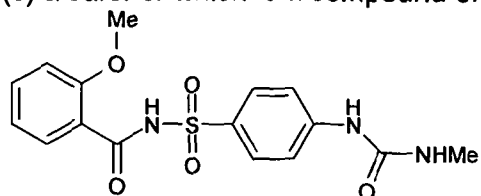
wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine;

20 and

(b) metazosulfuron or halosulfuron-methyl or an agriculturally acceptable salt thereof (preferably metazosulfuron or a salt thereof), and

- 27 -

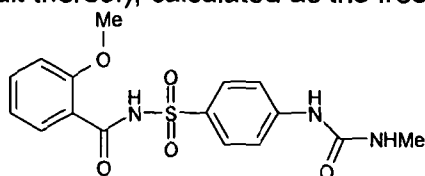
(c) a safener which is a compound of the following formula:



or which is cyprosulfamide.

Preferably, the weight ratio of the compound of formula (I) or salt thereof (e.g. Compound no. 1 or 2, or salt thereof), calculated as the free compound, to the safener (e.g. the compound

5



of formula , or cyprosulfamide) is from 20:1 to 1:2, more preferably from 8:1 to 1:2 (e.g. 8:1, 4:1 or 2:1), still more preferably from 4:1 to 1:1, e.g. 4:1 or 2:1.

10

The rate of application of safener in relation to herbicide depends largely on the method of application. In the case of field treatment, which is effected either using a tank mixture comprising a combination of safener and herbicide mixture or by separate application of safener and herbicide mixture, the ratio of the compound of formula (I) or salt (calculated as the free compound) to the safener is generally from 100:1 to 1:10, preferably from 20:1 to 1:1. In the case of field treatment, from 1 to 200 g of safener/ha, preferably from 5 to 100 kg of safener/ha, is generally applied.

15

In the composition according to the invention, the amounts of any oil additive which might be employed are generally from 0.01 to 2 %, based on the spray mixture. The oil additive can, for example, be added to the spray tank in the desired concentration after the spray mixture has been prepared.

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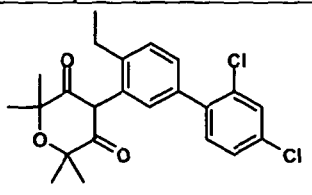
Some non-limiting examples of the present invention are disclosed in the following Formulation Examples and/or Biological Examples.

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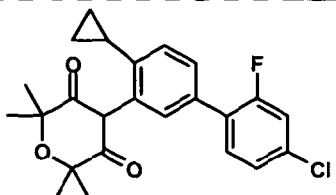
## FORMULATION EXAMPLES

## Formulation Example 1 - Emulsifiable concentrate (EC) formulation of Compound no. 1 (EC050 formulation)

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Ingredient (chemical structure/name or trade name)	Role	Chemical name	Grade	Concentration (g.l <sup>-1</sup> )
 (Compound no. 1)	Active ingredient (AI)			50
Emulsogen EL 360™	Emulsifier	castor oil ethoxylate	36 moles of ethylene oxide per mole of castor oil	94.7
Nansa EVM 63/B™	Emulsifier	calcium salt of dodecyl-benzene sulfonic acid	63 % in isobutanol	63.1
Soprophor BSU™	Emulsifier	tristyrylphenol ethoxylate	16 moles of ethylene oxide per mole of tristyrylphenol	31.6
N-octyl-2-pyrrolidone	Solvent	N-octyl-2-pyrrolidone		210.5
2-ethyl hexanol	Solvent	2-ethyl hexanol		to 1 litre

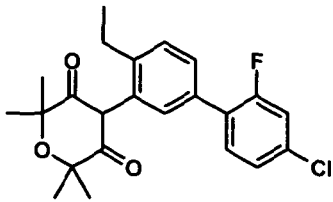
## Formulation Example 2 - Emulsifiable concentrate (EC) formulation of Compound no. 2 (EC050 formulation)

Ingredient (chemical structure / name or trade name)	Role	Chemical name	Grade	Concentration (g.l <sup>-1</sup> )
 (Compound no. 2)	Active ingredient (AI)			50

Emulsogen EL 360™	Emulsifier	castor oil ethoxylate	36 moles of ethylene oxide per mole of castor oil	84.4
Nansa EVM63/B™	Emulsifier	calcium salt of dodecyl-benzene sulfonic acid	63 % in isobutanol	42.2
acetophenone	Solvent	methyl-phenylketone		102.9
Solvesso 200™	Solvent	mixture of heavy aromatic hydrocarbons	ultra low naphthalene content	to 1 litre

**Formulation Example 3 - Emulsifiable concentrate (EC) formulation of Compound no. 3 (EC050 formulation)**

5

Ingredient (chemical structure/name or trade name)	Role	Chemical name	Grade	Concentration (g.l <sup>-1</sup> )
 <p>(Compound no. 3)</p>	Active ingredient (AI)			50
Emulsogen EL 360™	Emulsifier	castor oil ethoxylate	36 moles of ethylene oxide per mole of castor oil	95
Nansa EVM 63/B™	Emulsifier	calcium salt of dodecyl-benzene sulfonic acid	63 % in isobutanol	63.3
Soprophor BSU™	Emulsifier	tristyrylphenol ethoxylate	16 moles of ethylene oxide per mole of tristyrylphenol	31.7
N-octyl-2-pyrrolidone	Solvent	N-octyl-2-pyrrolidone		211.1
2-ethyl-hexanol	Solvent	2-ethyl hexanol		to 1 litre

**Emulsifiable concentrate (EC) procedure (used for Formulation Examples 1, 2 and 3)**

The solvent(s) are added to the vessel, followed by the emulsifiers. The mixture is rolled until a clear solution is obtained. The active ingredient is then added, and rolled till a clear solution is obtained.

**Formulation Example 4 - Emulsifiable concentrate (EC) formulation containing Compound no. 1 and metazosulfuron**

10 Formulation Example 4 is a variation of Formulation Example 1 in which, in the emulsifiable concentrate (EC), in addition to Compound no. 1, there is present metazosulfuron, and wherein Compound no. 1 and the metazosulfuron are present in the following weight ratios:

15 Formulation Example 4: weight ratio of Compound no. 1 to metazosulfuron is: 60:100, 90:100, 120:100, 60:90, 90:90, 120:90, 60:60, 90:60, 120:60, 60:45, 90:45, 120:45, 60:22, 90:22, or 120:22.

**Formulation Example 5 - Emulsifiable concentrate (EC) formulation containing Compound no. 2 and metazosulfuron**

20 Formulation Example 5 is a variation of Formulation Example 2 in which, in the emulsifiable concentrate (EC), in addition to Compound no. 2, there is present metazosulfuron, and wherein Compound no. 2 and the metazosulfuron are present in the following weight ratios:

25 Formulation Example 5: weight ratio of Compound no. 2 to metazosulfuron is: 60:100, 90:100, 120:100, 60:90, 90:90, 120:90, 60:60, 90:60, 120:60, 60:45, 90:45, 120:45, 60:22, 90:22, or 120:22.

**Formulation Example 6 - Emulsifiable concentrate (EC) formulation containing Compound no. 3 and metazosulfuron**

35 Formulation Example 6 is a variation of Formulation Example 3 in which, in the emulsifiable concentrate (EC), in addition to Compound no. 3, there is present metazosulfuron, and wherein Compound no. 3 and the metazosulfuron are present in the following weight ratios:

Formulation Example 6: weight ratio of Compound no. 3 to metazosulfuron is: 60:100, 90:100, 120:100, 60:90, 90:90, 120:90, 60:60, 90:60, 120:60, 60:45, 90:45, 120:45, 60:22, 90:22, or 120:22.



## BIOLOGICAL EXAMPLES

Test plants (rice and weeds) were grown in a glasshouse (greenhouse) under hot and humid conditions, and the application of various herbicides and herbicidal mixtures were tested:

- 5 - by post-emergence foliar spray application to rice or weeds (see Biological Example 1 below); and  
 - by post-emergence application to the floodwaters of transplanted flooded rice or to the floodwaters of flooded weeds (see e.g. Biological Example 2 below).

### 10 **Biological Example 1 – Glasshouse test for post-emergence foliar spray application of mixtures of compounds of formula (I) with either metazosulfuron or halosulfuron-methyl, to rice or weeds (test 106)**

#### ***Biological Example 1 – Materials and Methods***

15

- Herbicide Application: Post-emergence foliar spray application, 300 L/ha, single replicate
- Climate: Standard rice conditions (hot and humid), in glasshouse. Specifically, the glasshouse bay conditions were 30 °C/20°C day/night; 18/6 hours light/dark; 75% humidity.
- Rice: Rice seeds, variety IR-64 (an indica type of rice), were sown in seed trays. After about 7-8 days the resulting plants were transplanted into 6-inch-diameter circular pots with no holes containing Boughton loam soil, which was then saturated with water replicating swampy conditions. The herbicide application took place when the rice was at the 3-leaf 1-tiller growth stage – this was 9 days after transplantation.
- Weeds: Long thin troughs with no holes, containing five weed species in five different positions side-by-side in Boughton loam soil, were used, as follows; the herbicidal application took place at the shown growth stages:
  - *Echinochloa crus-galli* (ECHCG) - 2-3 leaves;
  - *Leptochloa chinensis* (LEFCH) - 2 leaves;
  - *Brachiaria plantaginina* (BRAPL) - 2 leaves;
  - *Scirpus juncooides* (SCPJU) - 2 leaves;
  - *Monochoria vaginalis* (MOOVA) - 2 leaves
- Soil used for weeds and rice: Boughton loam (clay soil, pH 7.0, 5.9% OM),
- Herbicidal compounds and compositions tested:
  - Compound no. 1 was tested in the form of EC050 Formulation Example 1
  - Compound no. 2 was tested in the form of EC050 Formulation Example 2
  - Compound nos. 1 and 2 were each tested at 15, 60, 90 & 120 g/ha on the weeds, and 60, 90, 120 & 240 g/ha on the rice; and were each tested alone or in combination with: 45g/ha metazosulfuron (technical sample, i.e. unformulated compound, NC-620), or 20g/ha halosulfuron-methyl (WG75 water-dispersible granule formulation, marketed by Nissan under the trade marks PERMIT™ or SERVIAN™).

40

- In addition, a single rate of 90g/ha of each of Compound nos. 1 and 2 was tested in combination with a lower rate of each sulfonyleurea: 22g/ha metazosulfuron (technical sample, i.e. unformulated compound, NC-620), or 10g/ha halosulfuron-methyl (WG75 water-dispersible granule formulation).
- The sulfonyle ureas were also tested alone at the higher rate (45g/ha metazosulfuron, or 20g/ha halosulfuron-methyl).
- All herbicidal treatments were applied with the adjuvant Adsee at 0.2%v/v.

### **Biological Example 1 - Overview of the General Materials and Greenhouse**

#### **10 (Glasshouse) Methods for Post-emergence Foliar Spray Application**

Rice seeds of variety IR-64 (an indica type of rice), were sown in seed trays. After about 7-8 days the resulting plants were transplanted into 6-inch-diameter circular pots with no holes containing Boughton loam soil. The loam soil in the rice pots was saturated with water replicating swampy conditions. The post-emergence foliar spray application of the herbicide(s) to the rice took place when the rice was at the 3-leaf 1-tiller growth stage – this was 9 days after transplantation and about 17 days after sowing.

The weeds, *Echinochloa crus-galli* (ECHCG), *Leptochloa chinensis* (LEFCH), *Brachiaria plantaginea* (BRAPL), *Scirpus juncooides* (SCPJU) and *Monochoria vaginalis* (MOOVA), were sown in seed trays (troughs) containing Boughton loam soil saturated with water, replicating swampy conditions. The rice and the weeds were then sprayed with the test herbicide(s) when they reached the growth stages mentioned above.

25 Glasshouse bay conditions were 30 °C/20°C day/night; 18/6 hours light/dark; 75% humidity.

The test herbicidal solutions were prepared by mixing the appropriate aliquots of the test substance and adjuvant (Adsee at 0.2%v/v) in de-ionised water to give the desired treatment concentration.

30

The herbicidal application was made as a foliar spray, using a tracksprayer. 2 days after application the weed trays / troughs and rice pots were flooded to ca. 2-3 cm water depth, and maintained at this level for the duration of the test.

35 A visual assessment of the % herbicidal damage was made 8 and 15 Days After herbicide Application (DAA), and the results are presented herein as % visual herbicidal damage where 0 = no damage to plants and 100 = total kill.

**Biological Example 1 – Some Specific Notes on Materials and Methods Actually Used**

1. Weeds were initially grown in biodegradable troughs / trays, however these started leaking 1 week prior to spray application. The weeds along with soil they had rooted into  
5 were transferred with as little disturbance as possible, into plastic troughs. The weeds continued to grow well and did not appear to be checked in their growth due to this change.

2. The pots of rice and troughs /trays of weeds were mistakenly flooded 1-2 days prior to the herbicidal spray application. An attempt was made to remove this flood water (leaving wet  
10 swampy soil) just before the foliar spray application of the herbicide(s). Pots and troughs were then flooded 2 days after the spray application of the herbicide(s). The rice and weeds were then grown on, in the same hot and humid glasshouse conditions, and were generally watered once or twice daily, generally keeping the flood water at a depth of ca. 2 – 3 cm in the pots and troughs.

3. Metazosulfuron, which was pure active ingredient (labelled as 'Technical' in the following results table), was prepared for the glasshouse test by dissolving in 10.56% Emulsogen EL  
15 <sup>TM</sup> (castor oil ethoxylate, CAS Registry number 61791-12-6), 42.22% *N*-methylpyrrolidone and 42.22% dipropylene glycol mono-ethyl ether to give a stock solution containing 5% of the test substance and 95% of (Emulsogen EL <sup>TM</sup>, *N*-methylpyrrolidone and dipropylene glycol mono-ethyl ether).  
20

4. The *Scirpus juncooides* (SCPJU) controls varied, so any results of 0 to 40% phytotoxicity versus SCPJU should be treated with caution.

**Biological Example 1 – Results****8 DAA (8 Days After herbicidal Application)**

Trends were similar at 8 DAA to those described below at 15 DAA.

**15 DAA (15 Days After herbicidal Application)**

The results at 15 DAA are illustrated in Table 1 below. A commentary then follows.

Table 1 – Biological Example 1 – Results (NT = not tested)

				Species and growth stage at application (numbers are % damage to the plant species at 15 DAA)					
Compound of formula (I)	Sulfonyl urea mixture partner	Applic- ation rate, comp- ound of formula (I) (g / ha)	Applic- ation rate, sulfonyl urea (g / ha)	Rice IR-64, 3 leaf & 1 tiller	ECH CG, 2-3 leaf	LEF CH, 2 leaf	BRA PL, 2 leaf	SCP JU, 2 leaf	MOO VA, 2 leaf
Compound no. 1 (EC050, Formulation Example 1)	None	15	-	NT	55	10	20	0	0
Compound no. 1 (EC050)	None	60	-	5	100	5	30	0	0
Compound no. 1 (EC050)	None	90	-	0	100	35	88	20	0
Compound no. 1 (EC050)	None	120	-	5	100	30	75	20	0
Compound no. 1 (EC050)	None	240	-	30	NT	NT	NT	NT	NT
Compound no. 1 (EC050, Formulation Example 1)	metazo- sulfuron (Technical)	15	45	NT	60	0	75	100	100
Compound no. 1 (EC050)	metazo- sulfuron	60	45	0	80	10	70	100	95
Compound no. 1 (EC050)	metazo- sulfuron	90	45	5	90	15	60	97	95
Compound no. 1 (EC050)	metazo- sulfuron	120	45	10	90	10	65	90	97
Compound no. 1 (EC050)	metazo- sulfuron	240	45	10	NT	NT	NT	NT	NT
Compound no. 1 (EC050, Formulation Example 1)	halo- sulfuron- methyl (WG75 formul- ation)	15	20	NT	55	0	20	100	80

Compound no. 1 (EC050)	halo-sulfuron-methyl	60	20	10	100	0	30	95	70
Compound no. 1 (EC050)	halo-sulfuron-methyl	90	20	5	100	5	60	92	80
Compound no. 1 (EC050)	halo-sulfuron-methyl	120	20	0	100	20	95	90	65
Compound no. 1 (EC050)	halo-sulfuron-methyl	240	20	15	NT	NT	NT	NT	NT
Compound no. 1 (EC050)	metazo-sulfuron	90	22	5	88	5	65	97	97
Compound no. 1 (EC050)	halo-sulfuron-methyl	90	10	10	100	0	65	85	50
Compound no. 2 (EC050, Formulation Example 2)	None	15	-	NT	75	0	10	10	0
Compound no. 2 (EC050)	None	60	-	0	100	5	78	20	0
Compound no. 2 (EC050)	None	90	-	0	100	5	92	10	0
Compound no. 2 (EC050)	None	120	-	0	100	5	98	90	0
Compound no. 2 (EC050)	None	240	-	0	NT	NT	NT	NT	NT
Compound no. 2 (EC050, Formulation Example 2)	metazo-sulfuron (Technical)	15	45	NT	65	0	55	100	95
Compound no. 2 (EC050)	metazo-sulfuron	60	45	0	100	5	70	98	93
Compound no. 2 (EC050)	metazo-sulfuron	90	45	0	100	0	80	98	97
Compound no. 2 (EC050)	metazo-sulfuron	120	45	0	100	5	82	95	100
Compound no. 2 (EC050)	metazo-sulfuron	240	45	5	NT	NT	NT	NT	NT

Compound no. 2 (EC050, Formulation Example 2)	halo-sulfuron-methyl (WG75 formulation)	15	20	NT	50	0	0	90	88
Compound no. 2 (EC050)	halo-sulfuron-methyl	60	20	5	100	15	78	80	65
Compound no. 2 (EC050)	halo-sulfuron-methyl	90	20	5	100	10	93	95	93
Compound no. 2 (EC050)	halo-sulfuron-methyl	120	20	0	100	30	93	93	80
Compound no. 2 (EC050)	halo-sulfuron-methyl	240	20	10	NT	NT	NT	NT	NT
Compound no. 2 (EC050, Formulation Example 2)	metazo-sulfuron (Technical)	90	22	5	90	0	65	85	92
Compound no. 2 (EC050, Formulation Example 2)	halo-sulfuron-methyl (WG75 formulation)	90	10	0	0	0	30	75	40
None	metazo-sulfuron (Technical)	-	45	10	60	0	60	90	85
None	halo-sulfuron-methyl (WG75)	-	20	5	25	0	30	95	88

*Discussion of Results for Compound no. 1 at 15 DAA*

Rice:

- 5 240g/ha of Compound no. 1 caused 30% damage to the rice at 15 DAA. Neither of the sulfonyl ureas (45 g/ha metazosulfuron or 20g/ha halosulfuron-methyl) tested in combination with 240g/ha Compound no. 1 caused this much damage (maximum 15% phytotoxicity), thus implying they are having a safening effect. It should be noted that the score (30%) that this is based on was from just one pot of rice to which 240g/ha Compound no. 1 had been
- 10 applied.

Weeds:

Compound no. 1 alone achieved good control of ECHCG (control at 60g/ha), some activity on BRAPL (approx 80% at 90g/ha), and negligible activity on the remaining 3 weeds tested.

- 5 Addition of 45g/ha metazosulfuron to Compound no. 1 caused a slight reduction in ECHCG activity, a slight improvement to BRAPL activity (at low Compound no. 1 rates), and a large improvement to SCPJU and MOOVA activity.

- 10 Addition of 20g/ha halosulfuron-methyl to Compound no. 1 did not reduce the herbicidal activity of Compound no. 1 against ECHCG, but was generally less effective than metazosulfuron at controlling SCPJU, BRAPL and particularly MOOVA.

Overall, all two mixtures gave similar efficacy.

- 15 The lower (22 g/ha) metazosulfuron rate in admixture with 90g/ha Compound no. 1 gave virtually identical results to the higher (45 g/ha) metazosulfuron rate.

- 20 The lower (10 g/ha) halosulfuron-methyl rate in admixture with 90g/ha Compound no. 1 gave lower activity on the MOOVA than mixtures with the higher (20 g/ha) halosulfuron-methyl rate.

*Discussion of Results for Compound no. 2 at 15 DAA*Rice:

- 25 Compound no. 2 alone showed no rice damage. The addition of the sulfonyl ureas caused negligible damage.

Weeds:

- 30 Compound no. 2 alone achieved good control of ECHCG, marginally better than Compound no. 1, also reasonable control of BRAPL (92% at 120g/ha, again better than Compound no. 1), and also control of SCPJU at 120g/ha.

Addition of 45g/ha metazosulfuron to Compound no. 2 improved Compound no. 2's weed spectrum by adding control of SCPJU and MOOVA at low rates.

Addition of 20g/ha halosulfuron-methyl caused some slight reduction of activity against ECHCG but only at 15g/ha Compound no. 2. Addition of 20g/ha halosulfuron-methyl improved the weed spectrum by giving good activity on SCPJU and MOOVA.

- 5 The lower (22 g/ha) metazosulfuron rate in combination with 90g/ha Compound no. 2 gave very slightly lower weed herbicidal activity than the higher (45 g/ha) metazosulfuron rate. Halosulfuron-methyl scores were inconsistent and thus not considered here.

*Discussion of Results for metazosulfuron or halosulfuron-methyl mixture partners at 15 DAA*

10

45g/ha metazosulfuron alone controlled ECHCG, SCPJU and MOOVA and gave reasonable activity on BRAPL. Application of 45g/ha metazosulfuron with Compound no. 1 or Compound no. 2 improved ECHCG activity and gave a slight increase in BRAPL activity, though LEFCH was still not fully controlled.

15

20g/ha halosulfuron-methyl alone was not as good, giving slight damage on BRAPL and MOOVA, and almost controlling SCPJU. Addition of either Compound no. 1 or Compound no. 2 to the 20g/ha halosulfuron-methyl vastly improved ECHCG control as well as improving activity on BRAPL, SCPJU and MOOVA, achieving control of 3-4 weed species.

20

***Biological Example 1 – Conclusions***

In this glasshouse test, Compound no. 2 was safer to rice and more active on the weeds (ECHCG, BRAPL and SCPJU) than Compound no. 1, under the conditions tested.

25

There is the possibility of safening of Compound no. 1 damage to rice, especially at higher (e.g. 240 g/ha) application rates, by applying in mixture with metazosulfuron or halosulfuron-methyl.

30

Mixtures of 15 to 240 g/ha of Compound no. 1 together with 45 g/ha of metazosulfuron, and of 90 g/ha Compound no. 1 + 22 g/ha metazosulfuron, were observed to have low (0-10%) phytotoxicity on the IR-64 indica rice, under the glasshouse conditions tested.



- 40 -

Mixtures of 15 to 240 g/ha of Compound no. 2 together with 45 g/ha of metazosulfuron, and of 90 g/ha Compound no. 2 + 22 g/ha metazosulfuron, were observed to have very low (0-5%) phytotoxicity on the IR-64 indica rice, under the glasshouse conditions tested.

- 5 The weed-control spectrum of Compound no. 1 and Compound no. 2 is increased and improved by inclusion of each of the two sulfonyl urea mixture partners, but no mixtures fully controlled LEFCH.

10 It is also noted that each of Compound no. 1 and Compound no. 2 alone have post-emergent herbicidal activity against BRAPL.

**Biological Example 2 - Glasshouse test for post-emergence floodwater application of mixtures of compounds of formula (I) with either metazosulfuron or halosulfuron-methyl, to flooded transplanted rice or to flooded weeds (test 105)**

**5 *Biological Example 2 - Overview of the Materials and Methods of Greenhouse (glasshouse) for the Transplanted Rice (TPR) System, as used in this test***

Rice seeds, variety IR-64 (an indica type of rice), were sown in seed trays. After about 7 days the resulting plants were transplanted as 3 groups of 2 plants, into 6-inch-diameter  
10 circular pots containing a loam soil (here, Boughton loam (clay, pH 7.0, 5.9% OM)) saturated with water, replicating swampy conditions. These were grown on for a further 9 days in a glasshouse bay (under the following climatic conditions: 30/20°C day/night; 18/6 hours light/dark; 75% humidity).

15 The weeds, *Echinochloa crus-galli* (ECHCG), *Fimbristylis miliacea* (FIMMI); *Scirpus maritimus* (SCPMA) and *Monochoria vaginalis* (MOOVA) were sown in long thin seed trays (troughs), with the trays / troughs containing the different weed species in different positions side-by-side. The trays / troughs contained a loam soil (Boughton loam) saturated with water, replicating swampy conditions. The weeds were grown on in a glasshouse bay under  
20 the same climatic conditions as the rice.

All pots of rice and all trays / troughs of weeds were flooded to ca. 2-3 cm water depth on the day prior to application of the test herbicidal substances. The herbicidal treatments were applied 9 days after the rice was transplanted. Growth stages at time of herbicide application  
25 were as follows (note: activity vs ECHCG was tested at two different growth stages):

IR-64 Rice: 2-3 leaves and 1 tiller

ECHCG (section 1 of trays): 2-3 leaves

MOOVA (section 2 of trays): 1-2 leaves

30 FIMMI (section 3 of trays): 3 leaves

ECHCG (section 4 of trays): 0.5 to 1 leaves (early growth stage of ECHCG)

SCPMA (section 3 of trays): 3 leaves

Test solutions were prepared by mixing the appropriate aliquots of the test substances in  
35 de-ionised water to give the desired treatment concentration.

Most of the test substances were used as formulated products. Specifically, Compound no. 1 was applied as the EC050 formulation disclosed in Formulation Example 1 herein (EC = emulsifiable concentrate). Compound no. 2 was applied as the EC050 formulation disclosed in Formulation Example 2 herein. Halosulfuron-methyl was used as a WG75 water-dispersible granule formulation, marketed by Nissan under the trade marks PERMIT™ or SERVICAN™.

The test substance metazosulfuron, which was pure active ingredient (labelled as 'Technical' in the following results table), was prepared for testing by dissolving in 10.56% Emulsogen EL™ (castor oil ethoxylate, CAS Registry number 61791-12-6), 42.22% *N*-methylpyrrolidone and 42.22% dipropylene glycol mono-ethyl ether to give a stock solution containing 5% of the test substance and 95% of (Emulsogen EL™, *N*-methylpyrrolidone and dipropylene glycol mono-ethyl ether).

Application of the test substances was made by pipetting the required amount of the test solution or the test formulation gently into the flood water of the appropriate pot or tray/trough.

The test plants were then grown on in the same glasshouse conditions, and watered twice daily keeping the flood water at a depth of ca. 2 – 3 cm.

A visual assessment of the % herbicidal damage was made 7 & 14 Days After Application of the herbicide(s) (DAA), and the results are presented herein as % visual herbicidal damage, where 0 = no damage to plants and 100 = total kill.

For the weeds and the rice, for each herbicidal compound or mixture, and for each application rate, only one rice pot and one weed tray/trough was used. That is, there were no replicates.

### 30 ***Biological Example 2 - Results***

The results at 14 DAA are illustrated in Table 2 below. A commentary then follows.

Table 2 – Biological Example 2 – Results (NT = not tested)

The results below show % herbicidal damage to the plant species tested at 14 DAA.

Compound of formula (I)	sulfonyl urea herbicide	application rate for compound of formula (I) (g / ha)	application rate for sulfonyl urea (g / ha)	Species and growth stage at application (numbers are % damage to the plant species at 14 DAA)					
				IR-64 rice 2-3 leaf, 1 tiller	ECH CG 2-3 leaf	MOO VA 1-2 leaf	FIM MI 3 leaf	ECH CG 0.5-1 leaf	SCP MA 3 leaf
Compound no. 1 (EC050, Formulation Example 1)	none	60	-	NT	80	0	5	100	0
Compound no. 1 (EC050)	none	90	-	15	85	0	5	98	0
Compound no. 1 (EC050)	none	120	-	20	100	0	5	100	0
Compound no. 1 (EC050)	none	240	-	35	NT	NT	NT	NT	NT
Compound no. 1 (EC050)	none	480	-	55	NT	NT	NT	NT	NT
Compound no. 1 (EC050, Formulation Example 1)	metazo-sulfuron (Technical)	60	90	NT	70	98	100	80	95
Compound no. 1 (EC050)	metazo-sulfuron	90	90	10	80	98	100	90	95
Compound no. 1 (EC050)	metazo-sulfuron	120	90	20	70	98	100	75	95
Compound no. 1 (EC050)	metazo-sulfuron	240	90	missing result (chlorotic plant)	NT	NT	NT	NT	NT
Compound no. 1 (EC050)	metazo-sulfuron	480	90	50	NT	NT	NT	NT	NT

Compound no. 1 (EC050, Formulation Example 1)	halo-sulfuron-methyl (WG75 formulation)	60	20	NT	30	95	95	55	90
Compound no. 1 (EC050)	halo-sulfuron-methyl	90	20	20	60	90	100	65	M
Compound no. 1 (EC050)	halo-sulfuron-methyl	120	20	25	65	95	100	85	85
Compound no. 1 (EC050)	halo-sulfuron-methyl	240	20	30	NT	NT	NT	NT	NT
Compound no. 1 (EC050)	halo-sulfuron-methyl	480	20	50	NT	NT	NT	NT	NT
Compound no. 1 (EC050, Formulation Example 1)	metazo-sulfuron (Technical)	90	60	10	70	95	100	85	95
Compound no. 1 (EC050, Formulation Example 1)	halo-sulfuron-methyl (WG75 formulation)	90	15	30	55	98	100	90	75
Compound no. 2 (EC050, Formulation Example 2)	none	60		NT	85	0	0	90	0
Compound no. 2 (EC050)	none	90		10	98	0	5	100	0
Compound no. 2 (EC050)	none	120		20	98	0	5	100	0
Compound no. 2 (EC050)	none	240		20	NT	NT	NT	NT	NT
Compound no. 2 (EC050)	none	480		30	NT	NT	NT	NT	NT
Compound no. 2 (EC050, Formulation Example 2)	metazo-sulfuron (Technical)	60	90	NT	70	98	100	90	90
Compound no. 2 (EC050)	metazo-sulfuron	90	90	5	75	98	100	60	90

Compound no. 2 (EC050)	metazo-sulfuron	120	90	15	60	100	100	50	85
Compound no. 2 (EC050)	metazo-sulfuron	240	90	10	NT	NT	NT	NT	NT
Compound no. 2 (EC050)	metazo-sulfuron	480	90	10	NT	NT	NT	NT	NT
Compound no. 2 (EC050, Formulation Example 2)	halo-sulfuron-methyl (WG75 formulation)	60	20	NT	60	95	100	70	80
Compound no. 2 (EC050)	halo-sulfuron-methyl	90	20	5	85	95	100	85	70
Compound no. 2 (EC050)	halo-sulfuron-methyl	120	20	5	85	95	100	90	95
Compound no. 2 (EC050)	halo-sulfuron-methyl	240	20	15	NT	NT	NT	NT	NT
Compound no. 2 (EC050)	halo-sulfuron-methyl	480	20	30	NT	NT	NT	NT	NT
Compound no. 2 (EC050, Formulation Example 2)	metazo-sulfuron (Technical)	120	60	15	65	98	100	85	99
Compound no. 2 (EC050)	halo-sulfuron-methyl (WG75)	120	15	NC *	NC *	NC *	NC *	NC *	NC *
none	metazo-sulfuron (Technical)	-	60	10	85	98	100	85	95
none	metazo-sulfuron (Technical)	-	90	15	80	98	100	80	95
none	halo-sulfuron-methyl (WG75)	-	15	5	5	90	100	15	40
none	halo-sulfuron-methyl (WG75)	-	20	10	5	80	100	5	80

NT = not tested.

\* NC = results not considered. The results on the weeds for 120 g/ha of Compound no. 2 and 15 g/ha halosulfuron-methyl were clearly not consistent with other similar treatments, suggesting there may have been an error in chemical formulation for this specific treatment, and so the rice and weeds results have been removed and not considered where NC is shown.

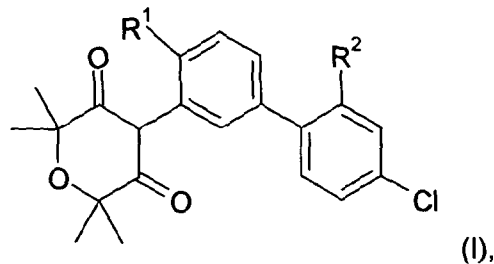
***Biological Example 2 - Comments on the results***

- 10 1. Inclusion of metazosulfuron as a mixture partner with either Compound no. 1 or Compound no. 2 gave a herbicidal composition with reasonably low rice phytotoxicity (damage). See for example the reasonably low rice phytotoxicity results for:
- (a) 90 g/ha metazosulfuron + 90-120 g/ha Compound no. 1,
  - (b) 60 g/ha metazosulfuron + 90 g/ha Compound no. 1,
  - 15 (c) 90 g/ha metazosulfuron + 90-480 g/ha Compound no. 2, and
  - (d) 60 g/ha metazosulfuron + 120 g/ha Compound no. 2.
2. There was a slight indication that metazosulfuron may reduce rice phytotoxicity (damage) caused by Compound no. 2.
- 20
3. Inclusion of either metazosulfuron or halosulfuron-methyl as a mixture partner with either Compound no. 1 or Compound no. 2 improved the weed control spectrum of the PRADO compound by achieving control of MOOVA, FIMMI and SCPMA.
- 25 4. Compound no. 2 (alone or in mixtures) was generally less damaging to rice than Compound no. 1 (under comparable conditions, alone or in mixtures), under the conditions tested.
- 30

**CLAIMS:**

1. A herbicidal composition comprising:  
 (a) a compound of formula (I) or an agriculturally acceptable salt thereof:

5



wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine;  
 and

- (b) metazosulfuron or an agriculturally acceptable salt thereof.

10

2. A herbicidal composition as claimed in claim 1, wherein, in the compound of formula (I) or the salt thereof, R<sup>1</sup> is ethyl.

- 15 3. A herbicidal composition as claimed in claim 2, wherein, in the compound of formula (I) or the salt thereof, R<sup>1</sup> is ethyl and R<sup>2</sup> is chlorine.

4. A herbicidal composition as claimed in claim 1, 2 or 3, wherein the compound of formula (I) or the salt thereof is present as the compound.

20

5. A herbicidal composition as claimed in claim 1, wherein, in the compound of formula (I) or the salt thereof, R<sup>1</sup> is cyclopropyl.

- 25 6. A herbicidal composition as claimed in claim 5, wherein, R<sup>1</sup> is cyclopropyl and R<sup>2</sup> is fluorine.

7. A herbicidal composition as claimed in claim 4, 5 or 6, wherein the compound of formula (I) or the salt thereof is present as the compound.

- 30 8. A herbicidal composition as claimed in any of the preceding claims, wherein the metazosulfuron or the salt thereof is present as the compound.



9. A herbicidal composition as claimed in any of the preceding claims, wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the free compound, to the metazosulfuron or the salt thereof, calculated as the free compound, is  
5 from 30:150 to 250:10.
10. A herbicidal composition as claimed in any of claims 1 to 8, wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the free compound, to the metazosulfuron or the salt thereof, calculated as the free compound, is from 50:120 to  
10 180:20.
11. A herbicidal composition as claimed in any of claims 1 to 8, wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the free compound, to the metazosulfuron or the salt thereof, calculated as the free compound, is from 80:120 to  
15 130:40.
12. A method of controlling weeds in crops of useful plants, which comprises applying a herbicidal composition of the invention, as defined in any one of claims 1 to 11, to the weeds and/or to the useful plants and/or to the locus thereof.  
20
13. A method as claimed in claim 12, wherein in the compound of formula (I) or the agriculturally acceptable salt thereof, R<sup>1</sup> is ethyl and R<sup>2</sup> is chlorine, or R<sup>1</sup> is cyclopropyl and R<sup>2</sup> is fluorine.
- 25 14. A method as claimed in claim 12 or 13, wherein the weeds and/or the useful plants and/or the locus thereof are flooded.
15. A method as claimed in claim 12, 13 or 14, wherein the herbicidal composition is applied post-emergence.  
30
16. A method as claimed in claim 12, 13, 14 or 15, wherein the crops of useful plants are rice.
17. A method as claimed in claim 16, wherein the rice is direct-seeded rice.  
35

18. A method as claimed in claim 12, 13, 14, 15, 16 or 17, wherein the herbicidal composition is applied post-emergence by foliar and/or spray application.

19. A method as claimed in claim 17 or 18, wherein the application rate for the compound of formula (I) or the agriculturally acceptable salt thereof, is from 30 to 150 g/ha of the compound of formula (I) or the salt thereof, calculated as the free compound.

20. A method as claimed in claim 17, 18 or 19, wherein the application rate for the metazosulfuron or the salt thereof is from 10 to 100 g/ha of the metazosulfuron or the salt thereof, calculated as the free compound.

21. A method as claimed in claim 17, 18, 19 or 20, wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the free compound, to the metazosulfuron or the salt thereof, calculated as the free compound, is from 45:75 to 130:15.

22. A method as claimed in claim 12, 13, 14 or 15, wherein the crops of useful plants are transplanted flooded rice.

23. A method as claimed in claim 22, wherein the herbicidal composition is applied to the flood-waters of the transplanted flooded rice at an application rate, for the compound of formula (I) or the salt thereof, of from 50 to 180 g/ha of the compound of formula (I) or a salt thereof, calculated as the free compound.

24. A method as claimed in claim 22 or 23, wherein the herbicidal composition is applied to the flood-waters of the transplanted flooded rice at an application rate, for the metazosulfuron or the salt thereof, of from 35 to 150 g/ha of the metazosulfuron or the salt thereof, calculated as the free compound.

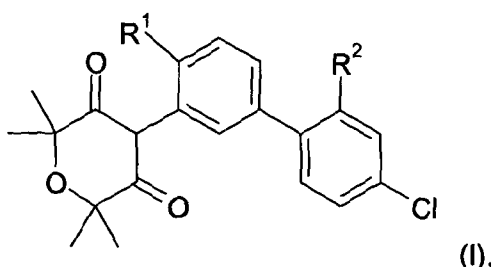
25. A method as claimed in claim 22, 23 or 25, wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the free compound, to the metazosulfuron or the salt thereof, calculated as the free compound, is from 50:120 to 180:40.

26. A method as claimed in any of claims 12 to 25, wherein the weeds to be controlled comprise: Echinochloa, Brachiaria, Leptochloa, Scirpus, Monochoria, Fimbristylis, and/or Cyperus.

27. A method as claimed in any of claims 12 to 25, wherein the weeds to be controlled comprise *Echinochloa* and/or *Brachiaria*.

5 28. A herbicidal composition comprising:

(a) a compound of formula (I) or an agriculturally acceptable salt thereof:



wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine;

10 and

(b) halosulfuron-methyl or an agriculturally acceptable salt thereof,

wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the free compound, to the halosulfuron-methyl or the salt thereof, calculated as the free compound, is from 30:60 to 250:3.

15

29. A herbicidal composition as claimed in claim 28, wherein, in the compound of formula (I) or the salt thereof, R<sup>1</sup> is ethyl and R<sup>2</sup> is chlorine, or R<sup>1</sup> is cyclopropyl and R<sup>2</sup> is fluorine.

20 30. A herbicidal composition as claimed in claim 28, wherein the weight ratio of the compound of formula (I) or the salt thereof, calculated as the free compound, to the halosulfuron-methyl or the salt thereof, calculated as the free compound, is from 50:40 to 180:5.

25 31. A method of controlling weeds in crops of useful plants, which comprises applying a herbicidal composition as defined in any of claims 28, 29 or 30 to the weeds and/or useful plants and/or to the locus thereof.

32. A method as claimed in claim 31, wherein:

30 the application rate, for the compound of formula (I) or the salt thereof, is from 50 to 180 g/ha of the compound of formula (I) or a salt thereof, calculated as the free compound; and

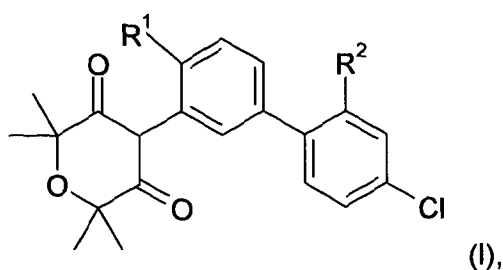
the application rate for the halosulfuron-methyl or the salt thereof is from 5 to 40 g/ha of the halosulfuron-methyl or the salt thereof, calculated as the free compound.

33. A method as claimed in claim 31 or 32, wherein the crops of useful plants are rice.

5

34. A herbicidal composition comprising:

(a) a compound of formula (I) or an agriculturally acceptable salt thereof:



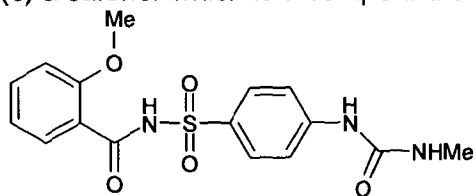
10

wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine;

and

(b) metazosulfuron or halosulfuron-methyl or an agriculturally acceptable salt thereof, and

(c) a safener which is a compound of the following formula:

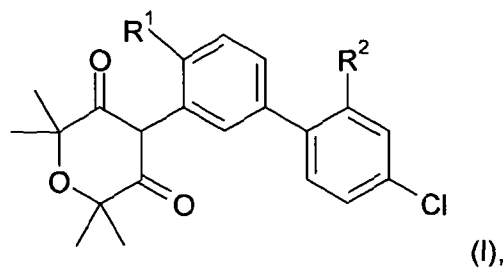


15

or which is cyprosulfamide.

35. A method of controlling Brachiaria weeds in crops of useful plants, which comprises applying a compound of formula (I):

20



wherein R<sup>1</sup> is ethyl or cyclopropyl, and R<sup>2</sup> is chlorine or fluorine;

or an agriculturally acceptable salt thereof, to the Brachiaria weeds or to the locus thereof.

36. A method as claimed in claim 35, wherein the compound of formula (I) or the salt thereof is applied to the Brachiaria weeds post-emergence.

5 37. A method as claimed in claim 35 or 36, wherein the compound of formula (I) or the salt thereof is applied at an application rate of from 50 to 180 g/ha of the compound of formula (I) or the salt thereof, calculated as the free compound.

38. A method as claimed in claim 35, 36 or 37, wherein the crops of useful plants are rice.

10

39. A method as claimed in any of claims 35 to 38, wherein the compound of formula (I) or the salt thereof is not applied to the Brachiaria weeds or to the locus thereof together with any of: fenoxasulfone, ipfencarbazone, propyrisulfuron, or *N*-[2-[(4,6-dimethoxy-1,3,5-triazin-2-yl)carbonyl]-6-fluorophenyl]-1,1-difluoro-*N*-methylmethanesulfonamide, or a salt of any of  
15 these.

20

## INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2011/000946

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. A01N47/36 A01N43/16 A01P13/00  
 ADD.

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)  
 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 practicable, search terms used)

EPO-Internal, WPI Data, 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.
Y	WO 2008/071405 A1 (SYNGENTA PARTICIPATIONS AG [CH]; SYNGENTA LTD [GB]; MUEHLEBACH MICHEL) 19 June 2008 (2008-06-19) cited in the application page 1, line 1 - page 3, line 9 page 31, lines 31-32 page 36, line 26 - page 37, line 12 page 62; example 7 pages 65-66; example 8 table A; compounds A-45, A-66, A-167 pages 233-237; examples A-B -----	1-27,34
Y	EP 1 748 047 A1 (NISSAN CHEMICAL IND LTD [JP]) 31 January 2007 (2007-01-31) paragraphs [0001], [0003] page 18; example 1 paragraph [0166] pages 59-61; examples 1-6; tables 3-8 ----- -/--	1-27,34



Further documents are listed in the continuation of Box C.



See patent family 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 application or patent 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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 March 2012

Date of mailing of the international search report

02/07/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
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Hateley, Martin

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB2011/000946

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-27(completely); 34(partially)

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2011/000946

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/304973 A1 (ROSINGER CHRISTOPHER HUGH [DE] ET AL) 2 December 2010 (2010-12-02) paragraphs [0003] - [0004] paragraphs [0007] - [0009] paragraph [0036] paragraphs [0044] - [0046] paragraph [0078]; compound B20 -----	1-27,34
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2011/000946

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**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-27(completely); 34(partially)

A herbicidal composition comprising a compound of formula (I), metazosulfuron and optionally a safener chosen from the group consisting of cyprosulfamide and N-(2-methoxybenzoyl)-4-[(methylaminocarbonyl)amino]benzenesulfonamide; and a method of controlling weeds in crops of useful plants using the said herbicidal composition

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2. claims: 28-33(completely); 34(partially)

A herbicidal composition comprising a compound of formula (I) and halosulfuron-methyl; and a method of controlling weeds using this herbicidal composition

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3. claims: 35-39

A method of controlling Brachiaria weeds in crops using a compound of formula (I)

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