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(54) Title: WEED CONTROL METHOD

(57) Abstract: The present invention relates to a method for controlling *Conyza sp.* at a locus said method comprising applying to the locus a synergistic amount of (i) bicyclopyrone; (ii) diquat and/or paraquat; and optionally (iii) a urea herbicide.

WEED CONTROL METHOD

The protection of crops from weeds and other vegetation which inhibit crop growth is a constantly recurring problem in agriculture. To help combat this problem, researchers in the field of synthetic chemistry have produced an extensive variety of chemicals and chemical formulations effective in the control of such unwanted growth. Chemical herbicides of many types have been disclosed in the literature and a large number are in commercial use.

In some cases, active herbicides have been shown to be more effective in combination than when applied individually. The result is often termed "synergism", since the combination demonstrates a potency or activity level exceeding that which it would be expected to have, based on knowledge of the individual potencies of the compounds.

Species of the genus *Conyza* are well known weeds. They include among others *Conyza bonariensis, Conyza canadensis, Conyza sumatrensis, Conyza ramosissima* and their various subspecies and synonyms. Strategies for controlling *Conyza sp.* have been reported, for example see Armel *et al.* (2009) Weed Technology 23:379-383. Some *Conyza* species (e.g. *C. bonariensis, C. canadensis, C. sumatrensis*) have developed resistance and multiple resistance to a range of herbicides, including glyphosate and therefore the provision of new methods by which *Conyza* sp. can be controlled effectively remains an important goal.

Thus, according to the present invention there is provided an improved method for controlling *Conyza sp.* at a locus said method comprising applying to the locus a synergistic amount of (i) bicyclopyrone (4-hydroxy-3-{2-[(2-methoxyethoxy)methyl]-6-(trifluoromethyl)-3-pyridylcarbonyl}bicyclo[3.2.1]oct-3-en-2-one); (ii) diquat and/or paraquat; and optionally (iii) a urea herbicide.

In a preferred embodiment of the present invention, components (i), (ii) and (iii) are all applied to the locus.

In another embodiment of the present invention component (ii) is paraquat.

In another embodiment the urea herbicide selected from the group consisting of chlorotoluron, dimefuron, diuron, flumeturon, isoproturon, isouron, karbutilate, linuron, methabenzthiazuron, metoxuron, monolinuron, neburon, siduron and tebuthiuron. Diuron is particularly preferred.

The rate of application of the herbicide components to the locus may vary within wide limits and depends on the nature of the soil, the method of application (pre-plant / pre-emergence , *etc.*), the crop plant, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. Typically bicyclopyrone is applied at a rate from 10 to 500 g ai/ha, preferably from 50 to 300 g ai/ha, and more preferably from 50 to 200 g ai/ha. Typically the diquat and/or paraquat can be applied from 50 to 3000 g ai/ha, preferably from 50 to 1000 g ai/ha. Typically, the urea herbicide is applied from 50 to 3000 g ai/ha, preferably from 150 to 1500 g ai/ha.

In another embodiment of the present invention the locus further comprises a crop plant. Examples of crop plants include, for example, cereals e.g. barley and wheat, cotton, oilseed rape, sunflower, maize, rice, soybeans, sugar beet, sugar cane and turf. Maize and soybeans are particularly preferred examples. Crops are to be understood as also including those crops which have been rendered tolerant to herbicides or classes of herbicides (e.g. ALS-, GS-, EPSPS-, PPO-, ACCase- and HPPD-inhibitors) by conventional methods of breeding or by genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding is Clearfield® summer rape (canola). Examples of crops that have been rendered tolerant to herbicides by genetic engineering methods include e.g. glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® and LibertyLink®.

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, or 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 comprising one or more genes that 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 or seed material thereof can be both resistant to herbicides and, at the same time, resistant to insect feeding ("stacked" transgenic events). For example, seed can have the ability to express an insecticidal Cry3 protein while at the same time being tolerant to glyphosate.

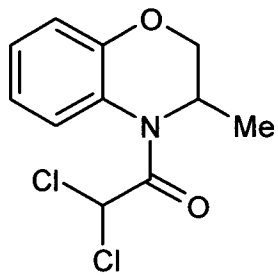
Crops are also to be understood to include those which are obtained by conventional methods of breeding or genetic engineering and contain so-called output traits (e.g. improved storage stability, higher nutritional value and improved flavour).

Where the locus comprises a crop plant it should be understood that components (i), (ii) and optionally (iii) may be applied pre-planting of the crop plant (applied before the crop is planted at the locus) and/or pre-emergence of the crop plant (wherein the crop has been planted at the locus but not yet emerged from the soil surface). It is preferred that components (i), (ii) and (iii) are applied to the locus pre-planting of the crop plant. It should be further understood that components (i), (ii) and optionally (iii) may be applied pre- or post-emergence of the *Conyza* sp. at the locus, preferably post-emergence – wherein the *Conyza* may be typically between 10 and 100 cm in height.

Components (i), (ii) and optionally (iii) may be applied simultaneously or in succession to the locus. The order of the compounds, in the event the application of the compounds is in succession, is not critical and the second compound is normally applied within preferably 2, more preferably 1, especially 0.5, days of the first compound. It is preferred, however, that components (i), (ii) and optionally (iii) are applied to the locus simultaneously in a combined herbicide composition. The amount and ratio of components a

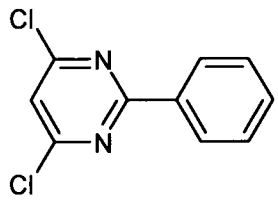
(i) and (ii) in the combined herbicide composition can vary depending on whether the composition is, for example, a pre-mix concentrate or a tank mixture. Preferably the weight ratio of compound (i) to compound (ii) is in the range of from 1:0.1 to 1:100, more preferably from 1:0.5 to 1:10 (w/w). Where component (iii) is present the ratio of (i) : (ii) : (iii) is preferably from 1 : 0.1 : 0.1 to 1 : 100 : 100 preferably from 1 : 1 : 1 to 1 : 10 : 10.

It should also be appreciated that one or more additional pesticides e.g herbicides, herbicide safeners, plant growth regulators, fertilizers, insecticides and/or fungicides, may in addition be applied to the locus in the method of the present invention. In an especially preferred embodiment a herbicide safener is applied in addition to the locus. Preferably, the herbicide safener is selected from the group consisting of a compound of formula 3.1



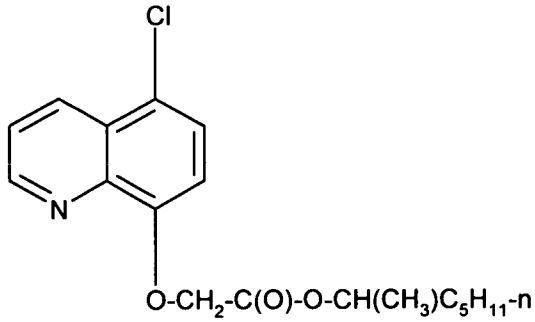
(3.1),

a compound of formula 3.2



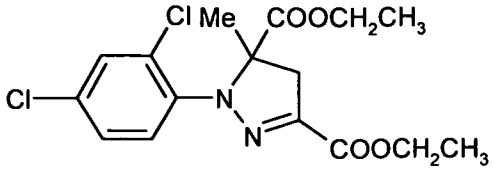
(3.2),

A compound of formula 3.3



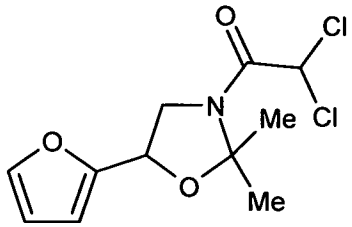
(3.3),

a compound of formula 3.4



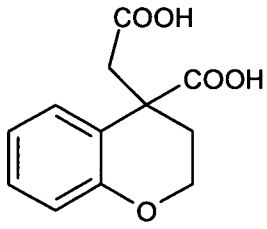
(3.4),

a compound of formula 3.5



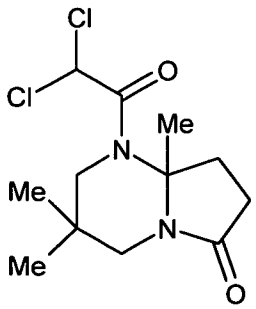
(3.5),

a compound of formula 3.6



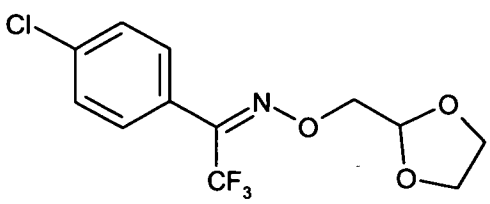
(3.6),

a compound of formula 3.7



(3.7),

a compound of formula 3.8

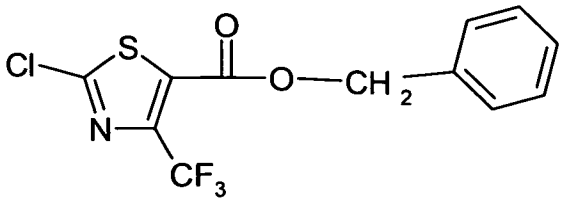


(3.8),

a compound of formula 3.9

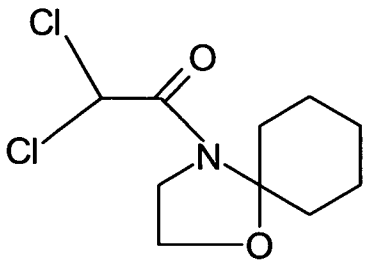
$Cl_2CHCON(CH_2CH=CH_2)_2$ (3.9),

a compound of formula 3.10



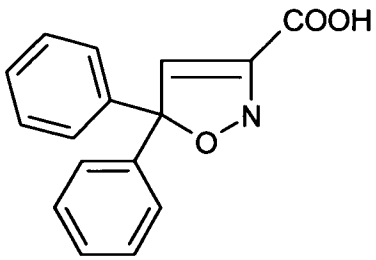
(3.10),

a compound of formula 3.11



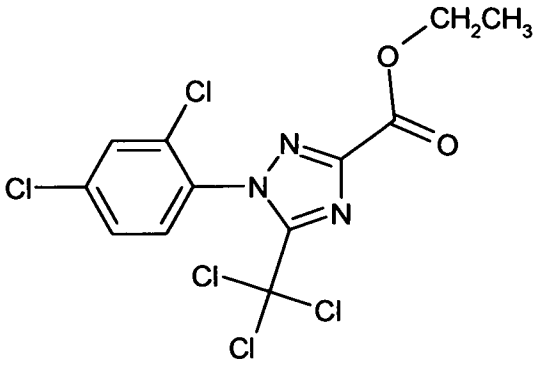
(3.11),

and of formula 3.12



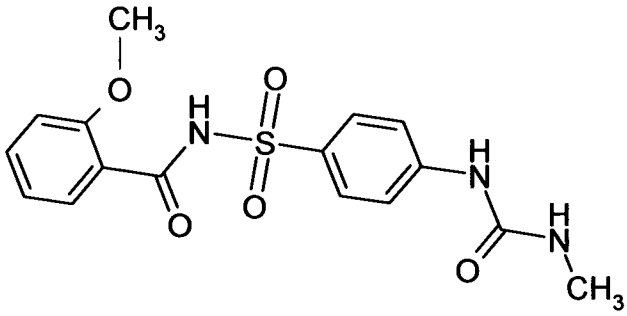
(3.12) and the methyl and ethyl esters and salts thereof,

a compound of formula 3.13



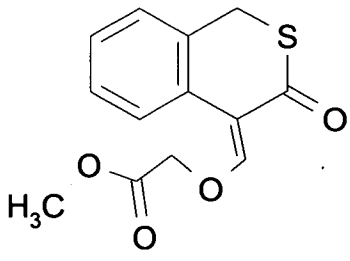
(3.13),

a compound of formula 3.14



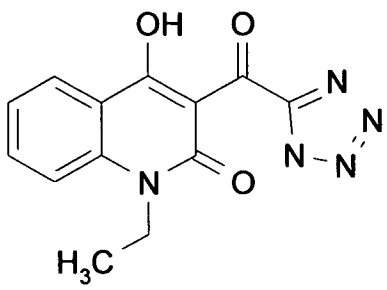
(3.14),

a compound of formula 3.15



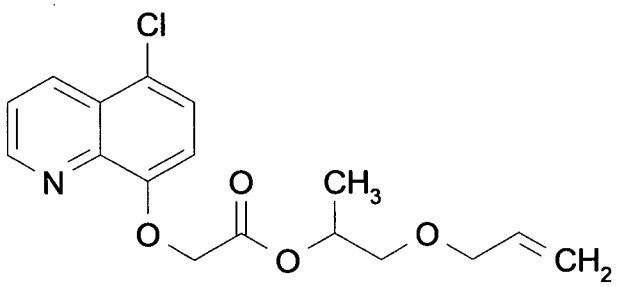
(3.15),

a compound of formula 3.16



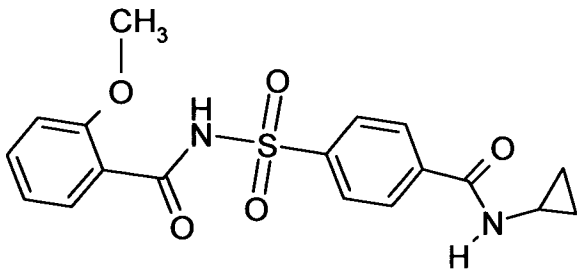
(3.16)

a compound of formula 3.17



(3.17).

and a compound of formula 3.18



(3.18)

The herbicidal composition will typically further comprise composition adjuvants conventionally used in formulation technology (also known as formulation auxiliaries), such as solvents, solid carriers or surfactants, for example, into emulsifiable concentrates, directly sprayable or dilutable solutions, wettable powders, soluble powders, dusts, granules or microcapsules, as described in WO 97/34483, pages 9 to 13. As with the nature of the formulation, the methods of application, such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the

prevailing circumstances. The formulations can be prepared in a known manner, *e.g.*, by intimately mixing and/or grinding the active ingredients with the formulation adjuvants, *e.g.*, solvents or solid carriers. In addition, surface-active compounds (surfactants) may also be used in the preparation of the formulations.

Examples of solvents and solid carriers are given, for example, in WO 97/34485, page 6. Depending on the nature of the active ingredients to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties. Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, in WO 97/34485, pages 7 and 8. Also suitable for the preparation of the herbicidal compositions according to the invention are the surfactants conventionally employed in formulation technology, which are described, *inter alia*, in "McCutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopaedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81.

The herbicidal formulations usually contain from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of active ingredients, from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant, and the balance a solid or liquid formulation adjuvant.

Whereas commercial products are usually formulated as concentrates (also known as pre-mix), the end user will normally employ dilute formulations. The compositions may also comprise further ingredients, such as stabilisers, *e.g.*, vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, *e.g.*, silicone oil, preservatives, viscosity regulators, binders, tackifiers and also fertilisers or other active ingredients.

Preferred formulations have especially the following compositions:
(% = percent by weight)

Emulsifiable concentrates:

active ingredient mixture:	1 to 90 %, preferably 5 to 20 %
surfactant:	1 to 30 %, preferably 10 to 20 %
liquid carrier:	balance

Dusts:

active ingredient mixture:	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 95 %

Suspension concentrates:

active ingredient mixture:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surfactant:	balance

Wettable powders:

active ingredient mixture:	0.5 to 90 %, preferably 1 to 80 %
surfactant:	0.5 to 20 %, preferably 1 to 15 %
solid carrier:	balance

Granules:

active ingredient mixture:	0.1 to 30 %, preferably 0.5 to 15 %
solid carrier:	99.9 to 70 %, preferably 99.5 to 85 %

Examples are specific formulations include:

F1. Emulsifiable concentrates	a)	b)	c)	d)
active ingredient mixture	5 %	10 %	25 %	50 %
calcium dodecylbenzenesulfonate	6 %	8 %	6 %	8 %
castor oil polyglycol ether (36 mol of ethylene oxide)	4 %	-	4 %	4 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	4 %	-	2 %

cyclohexanone	-	-	10 %	20 %
arom. hydrocarbon mixture C_9-C_{12}	85 %	78 %	55 %	16 %

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

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

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

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

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

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

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

F5. Coated granules	a)	b)	c)
active ingredient mixture	0.1 %	5 %	15 %
polyethylene glycol MW 200	1.0 %	2 %	3 %
highly dispersed silicic acid	0.9 %	1 %	2 %
inorganic carrier (diameter 0.1 - 1 mm) *e.g.*, $CaCO_3$ or SiO_2	98.0 %	92 %	80 %

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

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

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

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

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

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

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

It is often more practical for the active ingredients of the combinations according to the invention to be formulated separately and to be brought together in the desired mixing ratio in the applicator in the form of a "tank mixture" in water shortly before application. Alternatively, a pre-mix composition containing compounds (a) and (b) are formulated together.

Examples

Example 1.

Description of Test.

Field tests are carried out to determine the efficacy of the weed control method. Bicyclopyrone is provided as a 200 g/l SL. Paraquat is provided as "Gramoxone™" and paraquat and diuron are provided as "Gramocil™". Herbicide applications are made post-emergence to *Conyza sp.* 40 – 90 cm in height. All Bicyclopyrone treatments are made in conjunction with 0.5% v/v mineral oil. Plants were visually assessed for % control at 60 days after application (DAA)

The data obtained are analysed by comparing the observed mean response for the mixture treatments with their expected response using the Colby formula shown below:

$$P_M = P_1 + P_2 - P_1.P_2/100$$

where P_M denotes the expected response of the mixture treatment and P_1 and P_2 denote the observed mean responses from each of the mixture components tested alone.

The test results (shown in Tables 1, 2 and 3) indicate that synergy exists when bicyclopyrone is applied to *Conyza* in conjunction with (i) paraquat and (ii) paraquat + diuron.

Trt.	Herbicide	Rate (gAI/ha)	Mixture Partner	% Control		
				Obs.	Exp.	Diff.
1	Bicyclopyrone	100		30		
2		200		75		
3	Paraquat + Diuron	400 + 200		7		
4	Bicyclopyrone	100	Paraquat (400 g/ha) + Diuron (200 g/ha)	75	35	**+40**
5		200		92	77	**+15**

Table 1 % *Conzya* (80-90 cm) control at 60 DAA relative to untreated control.

Trt.	Herbicide	Rate (gAI/ha)	Mixture Partner	% Control		
				Obs.	Exp.	Diff.
1	Bicyclopyrone	150		75		
2	Paraquat	400		60		
3	Paraquat + Diuron	400 + 200		60		
4	Bicyclopyrone	150	Paraquat (400 g/ha)	95	90	**+5**
5	Bicyclopyrone	150	Paraquat (400 g/ha) + Diuron (200 g/ha)	92	90	**+2**

Table 2 % *Conzya* (60-70 cm) control 60 DAA relative to untreated control.

Trt.	Herbicide	Rate (gAI/ha)	Mixture Partner	% Control		
				Obs.	Exp.	Diff.
1	Bicyclopyrone	100		65		
2	Paraquat + Diuron	400 + 200		50		
3	Bicyclopyrone	100	Paraquat (400 g/ha) + Diuron (200 g/ha)	97	83	+14

Table 3 % *Conzya* (40-50 cm) control 60 DAA relative to untreated control.

CLAIMS

1. A method for controlling *Conyza sp.* at a locus said method comprising applying to the locus a synergistic amount of (i) bicyclopyrone; (ii) diquat and/or paraquat; and optionally (iii) a urea herbicide.

2. A method according to claim 1, wherein (i), (ii) and (iii) are applied to the locus.

3. A method according to any one of the previous claims, wherein component (ii) is paraquat.

4. A method according to any one of the previous claims, wherein component (iii) is diuron.

5. A method according to any one of the previous claims, wherein the locus further comprises a crop plant and wherein (i), (ii) and (iii) are applied to the locus pre-planting of the crop plant.

6. A method according to claim 5, wherein the crop plant is maize or soybean.

7. A method according to any one of the previous claims, wherein (i) and (ii) and (iii) are applied to the locus in a single herbicidal composition.

8. A method according to any one of the previous claims, wherein the *Conyza sp.* is resistant to glyphosate.

9. A herbicidal composition comprising (i) bicyclopyrone; (ii) diquat and/or paraquat; and optionally (iii) a urea herbicide.