Title: METHOD OF CONTROLLING WEEDS

(57) Abstract: A method for securing prolonged control of the growth of weeds at a crop locus, said method comprising the pre-crop planting application thereto of an effective amount of: (a) a benzoyl cyclohexanedione herbicide which is a compound of formula (I) or an enolic tautomer thereof, or a geometric isomer of a said tautomer; or an agriculturally acceptable salt or metal complex or chelate thereof; and (b) a chloroacetamide herbicide selected from (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide), (2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide), [2-chloro-6'-ethyl-N-(2-methoxy-1-methyl)acet-o-toluidide] and [(RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methyl) acetamide], or an agriculturally acceptable salt thereof.
Method of controlling weeds

Background of the invention.

This invention relates to a method for controlling the growth of weeds comprising the application of a mixture of a benzylo cyclohexanedione herbicide and a chloroacetamide herbicide, for use in corn (Zea mays). Herbicidal benzylo cyclohexanedianones are disclosed in the literature, for example European Patent Publication No. 0186118. In particular U.S. Patent 5, 506, 196 discloses 2-(2'-nitro-4'-methyl sulfonylbenzoyl)-1,3-cyclohexanedione, also known as mesotrione.

Chloroacetamides are a class of compounds which are known to be suitable for various herbicidal purposes. These include for example, 2-chloroacetamide herbicides such as alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide), acetochlor (2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide), metolachlor (2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidide) and dimethenamid [(RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide] each of which are known from the Pesticide Manual 11th edition (British Crop Protection Council); and are used pre-emergence or early post-emergence as herbicides for controlling annual grasses and broad leaved weeds in maize, peanuts, soybeans and other crops.

The chloroacetamide herbicides metolachlor, alachlor, acetochlor and dimethenamid are typically used for the control of weeds found in maize (corn). The use of these compounds at high dose rates can present problems in terms of maize crop damage, as reported for example by Owen et al., Res. Rep. North Cent. Weed Science Society, Volume 46, page 316 (1989). The problem is particularly prevalent with acetochlor, and typically it is necessary to employ acetochlor in mixture with an antidotal agent.

Reduced-till or no-till practices and associated pre-plant burndown herbicide treatments using contact herbicides, especially glyphosate, to remove existing foliage prior to crop planting are in common use for corn growing. The critical weed-free period for corn is during the first four weeks following crop emergence, and weed competition during this period will reduce yields. The corn herbicides are then applied by pre-
plant incorporation, or pre- or post-emergence of the crop. Fertilizer is normally added in a separate operation prior to corn planting.

An object of the present invention is to provide a method for the preplant burndown control of weeds for reduced-till or no-till corn.

A further object of the present invention is to provide a long-term protection of the crop by residual control of annual weeds and thus provide a method which allows the farmer to avoid applying unnecessary further treatments of herbicide after the emergence of the crop, which allows the farmer maximum flexibility in deciding on a treatment programme.

A further object of the invention is to provide a method which may prevent weeds becoming resistant to glyphosate or glufosinate.

A further object of the invention is to provide a herbicide which combines a contact herbicide to remove foliage prior to planting, with a residual herbicide to provide control of weeds which may subsequently germinate.

A further object of the invention is to provide a method which allows more time to receive rainfall necessary to allow the herbicide to move from the soil surface to the zone where weed seeds germinate.

A further object of the invention is to provide a method which reduces the workload for the farmer at planting time, and by combining the application of the herbicide with fertilizer can eliminate trips over the field.

A further object of the invention is to provide a method which allows more time for degradation of the herbicide in the soil, thus reducing the risk of phytotoxicity to the following crop.

These and other objects which are achieved in whole or in part by the present invention, will become apparent from the following description.

**Description of the Invention**

The present invention provides a method for securing prolonged, e.g. preferably season-long, control of the growth of weeds at a crop locus, said method comprising the pre-crop planting application thereto of an effective amount of:
(a) a benzoyl cyclohexanedione herbicide which is a compound of formula (I):

![Chemical Structure](image)

(I)

or an enolic tautomer thereof, or a geometric isomer of a said tautomer; or an agriculturally acceptable salt or metal complex or chelate of the compound; and

(b) a chloroacetamide herbicide selected from alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide), acetochlor (2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide), metolachlor [2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidide] and dimethenamid [(RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide], or an agriculturally acceptable salt thereof.

In one embodiment, the above components (a) and (b) may be used in combination with:

(i) glyphosate or an agriculturally acceptable salt thereof; or
(ii) glufosinate or an agriculturally acceptable salt thereof, optionally in combination with atrazine (6-chloro-N²-ethyl-N⁴-isopropyl-1,3,5-triazine-2,4-diamine); or
(iii) a 4-benzoylisoxazole of formula (II):

![Chemical Structure](image)

(II)

wherein R is hydrogen, -CO₂R³ or -S(O)₃R³;

R¹ is cyclopropyl;
R² is selected from halogen (preferably chlorine or bromine), -S(O)ₚMe, C₁₋₄ alkyl, C₁₋₄ haloalkyl (preferably trifluoromethyl), C₁₋₄ alkoxy and C₁₋₄ haloalkoxy;

n is two or three; m and p are zero, one or two; and

R³ is C₁₋₄ alkyl.

The compound of formula (I) is 2-(2′-nitro-4′-methylsulfonylethoxy)-1,3-cyclohexanediol, also known as mesotrione.

Preferably the chloroacetamide herbicide is acetochlor.

Preferably the 4-benzoxyisoxazole is of formula (II) wherein R is hydrogen or -CO₂R³; the other symbols are as hereinbefore defined.

In formula (II) above, compounds in which n is three and the groups (R²)ₙ occupy the 2, 3 and 4-positions of the benzoyl ring; or in which n is two and the groups (R²)ₙ occupy the 2- and 4-positions of the benzoyl ring are preferred.

In formula (II) above, preferably one of the groups R² is -SO₂Me.

The most preferred 4-benzoxyisoxazole of formula (II) is 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethyl)benzoylisoxazole, known as isoxaflutole.

It is understood that in the present invention, the use of a chloroacetamide herbicide includes the use in combination with an antidotally effective amount of an appropriate antidote. Those skilled in the art will be familiar with antidotes which are suitable for use with chloroacetamide herbicides and can readily determine an antidotally effective amount for a particular compound. Among the preferred antidotes which can be used in the method of use of the invention are furilazole and dichlormid.

Glyphosate which is N-(phosphonomethyl)glycine, and its salts for example an alkali metal, isopropylammonium or trimesium (trimethylsulfonium) salt, are described in U.S. Patent Application No.3,799,758.
Glufosinate is 4-[hydroxy(methyl)phosphinoyl]-DL-homoalanine, which is commonly used as the ammonium salt, ammonium 4-[hydroxy(methyl)phosphinoyl]-DL-homoalaninate.

Atrazine is 6-chloro-N\(^2\)-ethyl-N\(^4\)-isopropyl-1,3,5-triazine-2,4-diamine, and is disclosed in for example in "The Pesticide Manual", 11th edition (British Crop Protection Council) as a selective herbicide.

Glyphosate is a non-selective foliar herbicide which has only been used as a total herbicide or under conditions where there is no growing crop foliage present (e.g. burn down / no-till).

The application of a benzoyl cyclohexanedione herbicide and chloroacetamide herbicide pre-crop planting in accordance with the invention provides a useful control of existing foliage to clear the area for crop planting in reduced-till or no-till practice. In addition, the pre-emergence application of the benzoyl cyclohexanedione herbicide allows the control of weeds with protracted germinating periods to be accomplished without the need for a subsequent post-emergence application of a herbicide. Typically, one single pre-crop planting application of the herbicidal components (a) and (b) as defined above, optionally together with additional component (i), (ii) or (iii) as defined above, is sufficient to achieve weed control throughout the entire crop season. The need for subsequent applications of herbicide is therefore avoided. The method of the invention thus preferably comprises one single pre-crop planting application of (a) and (b), optionally together with (i), (ii) or (iii), in the absence of any subsequent application of herbicide to the crop locus.

Weeds that may be controlled by the method of the invention include grass weeds, broad-leaf weeds and sedges.

Examples of grass weeds include Alopecurus myosuroides, Avena fatua, Digitaria sanguinalis, Echinochloa crus-galli, Sorghum bicolor, Eleusine indica and Setaria spp, e.g. Setaria faberii or Setaria viridis.

Examples of broad-leaf weeds include Abutilon theophrasti, Amaranthus retroflexus, Bidens pilosa, Chenopodium album, Galium aparine, Ipomoea spp, e.g. Ipomoea purpurea, Sesbania exaltata, Sinapis arvensis, Solanum nigrum and Xanthium strumarium.

An example of a sedge is Cyperus esculentus.
The corn species to which the method of the invention may be applied also include genetically modified varieties such as those which are tolerant to mesotrione, acetochlor, glyphosate or glufosinate, such as Round-up Ready™ and Liberty Link™ corn.

In general the application rate of the benzoyl cyclohexanedione herbicide is from about 75g/ha to about 305g/ha, preferably from about 100g/ha to about 305g/ha, more preferably from about 150g/ha to about 305g/ha; and the application rate of the chloroacetamide herbicide is from about 1344g/ha to about 3060g/ha. For mixtures which include glyphosate the application rate of the benzoyl cyclohexanedione herbicide is from about 75g/ha to about 305g/ha, preferably from about 100g/ha to about 305g/ha, more preferably from about 150g/ha to about 305g/ha; the application rate of the chloroacetamide herbicide is from about 1344g/ha to about 3360g/ha; and the application rate of glyphosate is from about 420g/ha to about 1680g/ha, preferably from about 560g/ha to about 1120g/ha.

For mixtures which include glufosinate optionally combined with atrazine, the application rate of the benzoyl cyclohexanedione herbicide is from about 75g/ha to about 305g/ha, preferably from about 100g/ha to about 305g/ha, more preferably from about 150g/ha to about 305g/ha; the application rate of the chloroacetamide herbicide is from about 1344g/ha to about 3360g/ha; the application rate of glufosinate is from about 290g/ha to about 409g/ha; and when atrazine is present the application rate of atrazine is from about 250g/ha to about 3360g/ha, preferably from about 280g/ha to about 3360g/ha, more preferably from about 1120g/ha to about 2240g/ha.

For mixtures which include a 4-benzoylisoxazole of formula (II), the application rate of the benzoyl cyclohexanedione herbicide is from about 75g/ha to about 305g/ha, preferably from about 100g/ha to about 305g/ha, more preferably from about 150g/ha to about 305g/ha; the application rate of the chloroacetamide herbicide is from about 1344g/ha to about 3360g/ha; and the application rate of the 4-benzoylisoxazole of formula (II) is from about 50g/ha to about 210g/ha.

It will be understood that the application rates used will depend on the soil type, the growth stage of the weeds, the climatic conditions, the
time of application, the type of weeds present, the crops and other parameters apparent to the skilled worker.

Glyphosate may be applied in its acid form or as a derivative thereof, such as the mono isopropylammonium salt, the sodium salt, trimesium (trimethylsulfoxonium) salt or a mixture thereof. Preferably the mono isopropylammonium salt is used.

Glufosinate is generally used as the ammonium salt.

Generally the weight ratio of benzoyl cyclohexanedione herbicide : chloroacetamide herbicide is from 1:40.8 to 0.227:1.

The application of the mixtures of the invention is normally made up to 30 days before planting of the crop.

The herbicidal compositions are generally formulated as granules, as wettable powders, as emulsion concentrates, as flowables, as solutions or as suspensions, and contain solid and liquid carriers, surface-active agents and adjuvants such as a crop oil concentrate, a non-ionic surfactant, ammonium sulphate or urea ammonium nitrate. The addition of about 1% of crop oil concentrate, or about 1% of crop oil concentrate and about 2.5% of urea ammonium nitrate is particularly beneficial.

Preferred herbicidal compositions according to the present invention are water-dispersible granules.

The compound of formula (I) may exist in enolic tautomeric forms that may give rise to geometric isomers around the enolic double bond. Furthermore in certain cases the chloroacetamide herbicides may exist as optical isomers and/or stereoisomers. All such forms and mixtures thereof are embraced by the present invention.

The compositions according to the present invention may be used in combination with a fertilizer.

Compositions comprising the compounds of formula (I) may be prepared according to the teaching of the prior art cited above or similar references.

The invention also provides a product comprising a benzoyl cyclohexanedione herbicide as defined above, or an agriculturally acceptable salt or metal complex or chelate thereof; and a chloroacetamide herbicide selected from (2-chloro-2',6'-diethyl-
N-methoxymethylacetonilide), (2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide), [2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidide] and [(RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide], or an agriculturally acceptable salt thereof. In one embodiment the product of the invention as defined above further comprises:

(i) glyphosate or a salt thereof; or
(ii) glufosinate or a salt thereof, optionally in combination with atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4-diamine); or
(iii) a 4-benzoyleisoxazole of formula (II) as defined above; for simultaneous, separate or sequential application in securing the prolonged control of the growth of weeds at a crop locus, being applied pre-crop planting.

The following non-limiting example illustrates the invention.

**EXAMPLE 1**

Mesotrione (100g/ha), acetochlor (1792g/ha) and ammonium sulphate (2.5% v/v) were mixed with water and applied to the foliage and soil surface of a field containing the following weed species: *Amaranthus retroflexus*, *Abutilon theophrasti*, *Ipomoea lacunosa* and *Setaria viridis*. Corn (*Zea mays*) was planted 7 days after application. Thirty two days after treatment a very good level of post-emergence control of the above weed species was observed, compared to an untreated control. Table 1 shows the post-emergence weed control provided by this and other mixtures of the invention. No maize damage was observed in this trial.

**Table 1**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Dose g ai/ha</th>
<th>% Weed control/ Weed species SETVI</th>
<th>IPOLA</th>
<th>ABUTH</th>
<th>AMARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesotrione</td>
<td>100</td>
<td>60</td>
<td>98</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>acetochlor</td>
<td>1792</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mesotrione +</td>
<td>100</td>
<td>100</td>
<td>94</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Treatment</td>
<td>Dose g ai/ha</td>
<td>% Weed control/ Weed species</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>SETVI</td>
<td>IPOLA</td>
<td>ABUTH</td>
<td>AMARE</td>
</tr>
<tr>
<td>mesotrione + acetochlor</td>
<td>100 1792</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td>mesotrione + acetochlor</td>
<td>624</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>92</td>
</tr>
</tbody>
</table>

The residual weed control was also assessed 32 days after treatment, and these results are shown in Table 2.
<table>
<thead>
<tr>
<th>Ingredient Combination</th>
<th>100</th>
<th>99</th>
<th>100</th>
<th>100</th>
<th>97</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesotrione + acetochlor + glufosinate</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>mesotrione + acetochlor + glufosinate + atrazine</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>mesotrione + acetochlor + isoxaflutole</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>99</td>
</tr>
</tbody>
</table>

An excellent level of residual weed control was observed for at least 32 days after treatment.
CLAIMS

1. A method for securing prolonged control of the growth of weeds at a crop locus, said method comprising the pre-crop planting application thereto of an effective amount of:
   (a) a benzoyl cyclohexanedione herbicide which is a compound of formula (I):

   \[
   \text{(I)}
   \]

   or an enolic tautomer thereof, or a geometric isomer of a said tautomer; or an agriculturally acceptable salt or metal complex or chelate thereof; and

   (b) a chloroacetamide herbicide selected from (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide), (2-chloro-N-ethoxymethyl-6'-ethylacet-o-toluidide), (2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidide) and ((RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide), or an agriculturally acceptable salt thereof.

2. A method according to claim 1 which comprises the additional application to the crop locus of:
   (i) glyphosate or an agriculturally acceptable salt thereof; or
   (ii) glufosinate or an agriculturally acceptable salt thereof, optionally in combination with (6-chloro-N\(^2\)-ethyl-N\(^4\)-isopropyl-1,3,5-triazine-2,4-diamine); or
   (iii) a 4-benzoxyisoxazole of formula (II):

   \[
   \text{(II)}
   \]
wherein R is hydrogen, -CO₂R³ or -SO₂Rᵣ⁺R³;

R¹ is cyclopropyl;

R² is selected from halogen (preferably chlorine or bromine), -SO₂Me, C₁₋₄ alkyl, C₁₋₄ haloalkyl (preferably trifluoromethyl), C₁₋₄ alkoxy and C₁₋₄ haloalkoxy;

n is two or three; m and p are zero, one or two; and

R³ is C₁₋₄ alkyl.

3. A method according to claim 1 or 2 in which the application rate of the benzoyl cyclohexanedione herbicide is from 75g/ha to 305g/ha; and the application rate of the chloroacetamide herbicide is from 1344g/ha to 3060g/ha.

4. A method according to claim 2 in which the application rate of the benzoyl cyclohexanedione herbicide is from 75g/ha to 305g/ha; the application rate of the chloroacetamide herbicide is from 1344g/ha to 3360g/ha; and the application rate of glyphosate is from 420g/ha to 1680g/ha.

5. A method according to claim 2 in which the application rate of the benzoyl cyclohexanedione herbicide is from 75g/ha to 305g/ha; the application rate of the chloroacetamide herbicide is from 1344g/ha to 3360g/ha; the application rate of glufosinate is from 290g/ha to 409g/ha; and when atrazine is present the application rate of atrazine is from 250g/ha to 3360g/ha.

6. A method according to claim 2 in which the application rate of the benzoyl cyclohexanedione herbicide is from 75g/ha to 300g/ha; the application rate of the chloroacetamide herbicide is from 1344g/ha to 3360g/ha; and the application rate of the 4-benzoylisoxazole of formula (II) is from 50g/ha to 210g/ha.

7. A method according to claim 1 or 2 in which the weight ratio of benzoyl cyclohexanedione herbicide : chloroacetamide herbicide is from 1:40.8 to 0.227:1.

8. A method according to any one of the preceding claims in which the chloroacetamide herbicide is acetochlor.
9. A method according to any one of claims 2, 6 or 8 in which the 4-benzoylisoxazole of formula (II) is 5-cyclopropyl-4-(2-
methylsulphonyl-4-trifluoromethyl)benzoylisoxazole.

10. A product comprising a benzoyl cyclohexanedione herbicide as defined in claim 1, or an agriculturally acceptable salt or metal complex or chelate thereof; and a chloroacetamide herbicide selected from (2-
chloro-2',6'-diethyl-N-methoxymethylacetanilide), (2-chloro-
N-ethoxymethyl-6'-ethylnacet-o-toluidide), [2-chloro-6'-ethyl-N-(2-
methoxy-1-methylethyl)acet-o-toluidide] and [(RS)-2-chloro-N-(2,4-
dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide], or an agriculturally acceptable salt thereof, for simultaneous, separate or sequential application in securing the prolonged control of the growth of weeds at a crop locus, being applied pre-crop planting.

11. A product according to claim 10 which further comprises:

(i) glyphosate or a salt thereof; or
(ii) glufosinate or a salt thereof, optionally in combination with atrazine (6-chloro-N\(^2\)-ethyl-N\(^4\)-isopropyl-1,3,5-triazine-2,4-diamine); or
(iii) a 4-benzoylisoxazole of formula (II) as defined in claim 2.