



(51) International Patent Classification:

A01N 39/04 (2006.01) A01N 43/40 (2006.01)

A01N 47/36 (2006.01) A01P 13/00 (2006.01)

(21) International Application Number:

PCT/IB2018/055716

(22) International Filing Date:

31 July 2018 (31.07.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201731028212 08 August 2017 (08.08.2017) IN

(71) Applicant: UPL LTD [IN/IN]; Agrochemical Plant, Durgachak, Midnapore Dist., West Bengal, Haldia 721 602 (IN).

(72) Inventors: BRITO, Alexandre Leite; UPL House, 610 B/2, Bandra Village, Off Western Express Highway, Bandra East, Maharashtra, Mumbai 400051 (IN). DE ALMEIDA, Bruna Mariele; UPL House, 610 B/2, Bandra Village, Off Western Express Highway, Bandra East, Maharashtra, Mumbai 400051 (IN). SILVA, Ferdinando Marcos Lima; UPL House, 610 B/2, Bandra Village, Off Western Express Highway, Bandra East, Maharashtra, Mumbai 400051 (IN). DA CUNHA, Joaquim Ribeiro; UPL House, 610 B/2, Bandra Village, Off Western Express Highway, Bandra East, Maharashtra, Mumbai 400051 (IN). HOHMANN, Luciano Zanotto; UPL House, 610 B/2, Bandra Village, Off Western Express Highway, Bandra East, Maharashtra, Mumbai 400051 (IN). GONÇALVES, Natalia; UPL House, 610 B/2, Bandra Village, Off Western Express Highway, Bandra East, Maharashtra, Mumbai 400051 (IN). DECARO JUNIOR, Sergio Tadeu; UPL House, 610 B/2, Bandra Village, Off Western Express Highway, Bandra East, Maharashtra, Mumbai 400051 (IN). SHROFF, Jaidev, Rajnikant; 206, Swiss Tower, Cluster Y, Jumeirah Lake Towers, P.O. Box: 33421, Dubai (AE). SHROFF, Vikram, Rajnikant; 206, Swiss Tower, Cluster Y, Jumeirah Lake Towers, P.O. Box: 33421, Dubai (AE).

(74) Agent: MAJUMDAR, Subhatosh et al.; 5, Harish Mukherjee Road, West Bengal, Kolkata 700 025 (IN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,

OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: SYNERGISTIC HERBICIDAL COMBINATIONS

(57) Abstract: A herbicidal combination comprising at least two synthetic auxins, or at least two synthetic auxins with at least one ALS inhibitor, a composition comprising these combinations, a method of use of these combinations and a kit comprising the components of these combinations.

## **SYNERGISTIC HERBICIDAL COMBINATIONS**

### **Technical Field**

The present invention relates to a herbicidal combination for controlling undesirable  
5 plants. The present invention more specifically relates to a synergistic combination  
of herbicides for controlling weeds.

### **Background and prior art**

Unwanted plants such as weeds effect soil resources available for cultivated crops  
10 and can lead to a decrease in yield and eventually crop loss. Modern herbicides  
are used to either control or suppress these undesirable plants so as to allow sown  
crops a greater share of nutrients. Farmers usually control these plants at the pre-  
plant stage as well as after sowing.

15 Current practices include combining herbicides with varied modes of action, which  
allows for broader spectrum of control and resistance management. The herbicidal  
effectiveness of a compound cannot be predicted from an examination of the  
substituent groups of the compound. Often quite closely related compounds  
possess different weed control abilities. Various herbicides of the same class of  
20 compounds may have complementary areas of activity and thus can be useful to  
control a variety of weeds upon application of a combination. Furthermore, the  
various herbicides are not completely effective so as to control all the infesting  
weeds in a field crop, which necessitates the use of herbicidal combinations.

25 Synthetic Auxins are used for controlling broadleaf weeds in grass crops, pastures,  
and industry. These are readily absorbed through both roots and foliage and  
translocate by phloem or xylem to meristematic tissue interfering with cell formation  
that results in abnormal root and shoot growth. Application of these herbicides  
results in the disruption of several growth processes in susceptible plants which  
30 likely affects cell wall plasticity and nucleic acid metabolism as well as protein  
synthesis, cell division and growth, and stimulate ethylene evolution, which may in

## 2

some cases produce the characteristic epinastic symptoms associated with exposure to these herbicides.

Picloram is a synthetic auxin which controls broadleaf weeds. Combination of  
5 Picloram with other herbicides are known from **WO2014093210A1 (Ovalle et.al)**  
or **WO2014202092A1 (Schlosser et.al)**. Ovalle et al teach a combination  
comprising picloram with aminocyclopyrachlor. Schlosser et al teach a combination  
comprising picloram and pethoxamid.

10 2,4-D is a synthetic auxin used for the control of broad-leaved weeds.  
Combinations of 2,4D with other herbicides are known in the prior art including  
glyphosate (WO2010123871 A1), glufosinate (WO2015089014 A1) and other  
herbicides.

15 Herbicides that inhibit acetolactate synthase (ALS) enzyme are broad spectrum  
herbicides. These herbicides are an excellent tool for controlling post emergent  
herbicide for broad leaf weed control in various crops.

Combinations of herbicides are used to control a broader range of weeds.  
20 However, the combination of herbicides may not always result in the desired effect.  
Combination of herbicides may lead to an additive effect or an antagonistic effect.  
It may also result in phytotoxicity to the crops making it an undesirable combination.  
Agronomists must therefore, carefully select the herbicides that can be combined  
to offer a synergistic effect that would control weeds while having no phytotoxic  
25 effect on the crop, and reduce the chances of development of herbicide resistant  
weeds. There still remains a need for improved herbicidal combinations that can  
effectively control weeds thereby improving yield and plant health, with reduced  
phytotoxicity.

30 There is therefore a need in the art for combinations that have advantageous  
properties such as an herbicidal combination that is synergistic, helps in resistance

management, reduces dosage of herbicides used thus causing minimal damage to the environment, or a herbicidal combination that has excellent residual effects.

Embodiments of the present invention may therefore ameliorate one or more of the  
5 above mentioned problems:

#### **Objects of the invention**

Therefore, one object of the present invention is to provide a synergistic herbicidal combination.

10

Another object of the present invention is to provide a method of controlling weeds at a locus by application of a synergistic herbicidal combination.

Another object of the present invention is to provide a composition comprising a  
15 synergistic herbicidal combination.

Another object of the present invention is to provide a method of controlling herbicide resistant weeds.

20 Yet another object of the present invention is to provide a method of increasing yield in a crop by application of a synergistic herbicidal combination.

Another object of the present invention is to provide a method of improving the plant health by application of a synergistic herbicidal combination.

25

Some or all these and other objects of the invention can be achieved by way of the invention described hereinafter.

#### **Summary of the invention**

30 A herbicidal combination comprising at least two synthetic auxin herbicides and at least one ALS inhibitor herbicide.

## 4

A method of controlling weeds at a locus, the method comprising applying a combination comprising at least two synthetic auxin herbicides and at least one ALS inhibitor herbicide to the locus.

- 5 A composition comprising at least two synthetic auxin herbicides; at least one ALS inhibitor herbicide and at least one agrochemically acceptable excipient.

A method of controlling weeds at a locus, said method comprising applying a composition comprising at least two synthetic auxin herbicides; at least one ALS  
10 inhibitor herbicide and at least one agrochemically acceptable excipient.

**Detailed Description of the invention**

The term herbicide, as used herein, shall mean an active ingredient that kills, controls or otherwise adversely modifies the growth of plants. As used herein, a  
15 herbicidally effective or vegetation controlling amount is an amount of active ingredient that causes a "herbicidal effect," i.e., an adversely modifying effect and includes deviations from natural development, killing, regulation, desiccation, or retardation. The terms "plants" and "vegetation" include, but are not limited to, germinant seeds, emerging seedlings, plants emerging from vegetative  
20 propagules, and established vegetation. The term "locus" as used herein shall denote the vicinity of a desired crop in which weed control, typically selective weed control is desired. The locus includes the vicinity of desired crop plants wherein the weed infestation has either emerged or is yet to emerge. The term crop shall include a multitude of desired crop plants or an individual crop plant growing at a  
25 locus.

The present inventors have found that the combination of herbicides belonging to classes of synthetic auxins with ALS inhibitor herbicides results in a synergistic control of undesirable plants, at the locus of the desirable crop plants.

## 5

Thus an embodiment of the present invention may be a herbicidal combination comprising at least two synthetic auxins and at least one ALS inhibitor herbicide.

The synthetic auxins of the present invention may be selected from (2,4-D); 2,4-  
5 DB; dicamba; chloramben; 2,4,5-T; clomeprop; dichlorprop; dichlorprop-P; MCPA; MCPB; mecoprop; aminopyralid; clopyralid; fluroxypyr; halauxifen-methyl; picloram; triclopyr; aminocyclopyrachlor; quinclorac; quinmerac and their salts; and esters thereof.

10 In an embodiment, the combination of the present invention comprises at least two synthetic auxins.

In an embodiment, the synthetic auxins of the present invention may be selected from the group consisting of 2,4-D and dicamba; 2,4-D and MCPA; 2,4-D and  
15 fluroxypyr; 2,4-D and halauxifen-methyl; 2,4-D and picloram; 2,4-D and triclopyr; 2,4-D and quinclorac; 2,4-D and quinmerac; dicamba and MCPA; dicamba and fluroxypyr; dicamba and halauxifen-methyl; dicamba and picloram; dicamba and triclopyr; dicamba and quinclorac; dicamba and quinmerac; MCPA and fluroxypyr; MCPA and halauxifen-methyl; MCPA and picloram; MCPA and triclopyr; MCPA  
20 and quinclorac; MCPA and quinmerac; fluroxypyr and halauxifen-methyl; fluroxypyr and picloram; fluroxypyr and triclopyr; fluroxypyr and quinclorac; fluroxypyr and quinmerac; halauxifen-methyl and picloram; halauxifen-methyl and triclopyr; halauxifen-methyl and quinclorac; halauxifen-methyl and quinmerac; picloram and triclopyr; picloram and quinmerac; picloram and quinclorac; triclopyr  
25 and quinclorac; triclopyr and quinmerac; and quinclorac and quinmerac.

In an embodiment, at least two synthetic auxins of the present invention are 2,4-D and picloram.

30 In an embodiment, at least two synthetic auxins of the present invention may be halauxifen-methyl and picloram.

## 6

In an embodiment, the synthetic auxins of the present invention may be a combination of 2,4-D, picloram and triclopyr.

ALS inhibitor herbicides cover a wide chemical class of compounds including  
5    sulfonyleureas, imidazolinones, triazolopyrimidines, and pyrimidinyl thiobenzoates.

In an embodiment, the ALS inhibitor herbicides are sulfonyleurea herbicides.

Sulfonyleurea herbicides are known in the art. Examples of such sulfonyleurea  
10    herbicides include rimsulfuron, metsulfuron, metsulfuron methyl, bensulfuron  
methyl, ethametsulfuron, nicosulfuron, triasulfuron, primisulfuron, bensulfuron,  
chlorimuron, chlorimuron-ethyl, chlorsulfuron, sulfometuron, thifensulfuron,  
tribenuron, triflurosulfuron, clopyrasulfuron and pyrazosulfuron.

15    Thus, an aspect of the present invention may provide synergistic combinations of:

- (a) at least two synthetic auxins selected from the group comprising (2,4-D),  
2,4-DB, dicamba, chloramben, 2,4,5-T, clomeprop, dichlorprop, dichlorprop-  
P, MCPA, MCPB, mecoprop, aminopyralid, clopyralid, fluroxypyr,  
halauxifen-methyl, picloram, triclopyr, aminocyclopyrachlor, quinclorac,  
20    quinmerac; and
- (b) at least one ALS inhibitor herbicide selected from sulfonyleurea herbicides.

Thus, in an embodiment, the sulfonyleurea herbicide may be selected from the  
group consisting of amidosulfuron, azimsulfuron, bensulfuron, chlorimuron,  
25    cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron,  
foramsulfuron, halosulfuron, imazosulfuron, mesosulfuron, metazosulfuron,  
methiopyrisulfuron, monosulfuron, nicosulfuron, orthosulfamuron, oxasulfuron,  
primisulfuron, propyrisulfuron, pyrazosulfuron, rimsulfuron, sulfometuron,  
sulfosulfuron, trifloxysulfuron, zuomihuanglong, chlorsulfuron, cinosulfuron,  
30    ethametsulfuron, iodosulfuron, iofensulfuron, metsulfuron, prosulfuron,  
thifensulfuron, triasulfuron, tribenuron, triflurosulfuron, and tritosulfuron.

Thus, an aspect of the present invention may provide synergistic combinations of:

- (a) a synthetic auxins combination selected from the group consisting of 2,4-D and dicamba; 2,4-D and MCPA; 2,4-D and fluroxypyr; 2,4-D and halauxifen-methyl; 2,4-D and picloram; 2,4-D and triclopyr; 2,4-D and quinclorac; 2,4-D and quinmerac; dicamba and MCPA; dicamba and fluroxypyr; dicamba and halauxifen-methyl; dicamba and picloram; dicamba and triclopyr; dicamba and quinclorac; dicamba and quinmerac; MCPA and fluroxypyr; MCPA and halauxifen-methyl; MCPA and picloram; MCPA and triclopyr; MCPA and quinclorac; MCPA and quinmerac; fluroxypyr and halauxifen-methyl; fluroxypyr and picloram; fluroxypyr and triclopyr; fluroxypyr and quinclorac; fluroxypyr and quinmerac; halauxifen-methyl and picloram; halauxifen-methyl and triclopyr; halauxifen-methyl and quinclorac; halauxifen-methyl and quinmerac; picloram and triclopyr; picloram and quinmerac; picloram and quinclorac; triclopyr and quinclorac; triclopyr and quinmerac; and quinclorac and quinmerac; and
- (b) a sulfonylurea herbicide selected from the group consisting of amidosulfuron, azimsulfuron, bensulfuron, chlorimuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, mesosulfuron, metazosulfuron, methiopyrisulfuron, monosulfuron, nicosulfuron, orthosulfamuron, oxasulfuron, primisulfuron, propyrisulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, trifloxysulfuron, zuomihuanglong, chlorsulfuron, cinosulfuron, ethametsulfuron, iodosulfuron, iofensulfuron, metsulfuron, prosulfuron, thifensulfuron, triasulfuron, tribenuron, triflusulfuron, and tritosulfuron.

In an embodiment, the sulfonylurea herbicide is metsulfuron methyl.

Therefore, an embodiment of the present invention may provide a combination comprising:

- (a) picloram;

(b) 2,4-D; and

(c) Metsulfuron methyl.

In an embodiment, the ALS inhibitor herbicide may be imidazolinone herbicide.

5

In an embodiment, the imidazolinone herbicide may be selected from the group consisting of imazamethabenz, imazamox, imazapic, imazapyr, imazaquin and imazethapyr.

10 In an embodiment, the ALS inhibitor herbicide may be triazolopyrimidine herbicide.

In an embodiment, the triazolopyrimidine herbicide may be selected from the group consisting of chloransulam, diclosulam, florasulam, flumetsulam, metosulam, penoxsulam and pyroxsulam.

15

In an embodiment, the ALS inhibitor herbicide may be a pyrimidinyl benzoic acid herbicide.

In an embodiment, the pyrimidinyl benzoic acid herbicide may be selected from  
20 bispyribac, pyriminobac and pyriithiobac.

In an embodiment, the combinations of the present invention include the following preferred combinations.

25 In an embodiment, each individual row appearing in the table below represents the combinations in an embodiment of the present invention.

| S No. | Synthetic auxin I | Synthetic auxin II | ALS inhibitor      |
|-------|-------------------|--------------------|--------------------|
| 1     | 2,4-D             | Dicamba            | Metsulfuron methyl |
| 2     | 2,4-D             | Dicamba            | Bensulfuron methyl |

|    |       |                   |                    |
|----|-------|-------------------|--------------------|
| 3  | 2,4-D | Dicamba           | Pyrazosulfuron     |
| 4  | 2,4-D | Dicamba           | Imazamox           |
| 5  | 2,4-D | Dicamba           | Imazapic           |
| 6  | 2,4-D | Dicamba           | Imazapyr           |
| 7  | 2,4-D | Dicamba           | Imazethapyr        |
| 8  | 2,4-D | Dicamba           | Penoxsulam         |
| 9  | 2,4-D | Dicamba           | Pyroxsulam         |
| 10 | 2,4-D | Dicamba           | Bispyribac         |
| 11 | 2,4-D | MCPA              | Metsulfuron methyl |
| 12 | 2,4-D | MCPA              | Bensulfuron methyl |
| 13 | 2,4-D | MCPA              | Pyrazosulfuron     |
| 14 | 2,4-D | MCPA              | Imazamox           |
| 15 | 2,4-D | MCPA              | Imazapic           |
| 16 | 2,4-D | MCPA              | Imazapyr           |
| 17 | 2,4-D | MCPA              | Imazethapyr        |
| 18 | 2,4-D | MCPA              | Penoxsulam         |
| 19 | 2,4-D | MCPA              | Pyroxsulam         |
| 20 | 2,4-D | MCPA              | Bispyribac         |
| 21 | 2,4-D | Fluroxypyr        | Metsulfuron methyl |
| 22 | 2,4-D | Fluroxypyr        | Bensulfuron methyl |
| 23 | 2,4-D | Fluroxypyr        | Pyrazosulfuron     |
| 24 | 2,4-D | Fluroxypyr        | Imazamox           |
| 25 | 2,4-D | Fluroxypyr        | Imazapic           |
| 26 | 2,4-D | Fluroxypyr        | Imazapyr           |
| 27 | 2,4-D | Fluroxypyr        | Imazethapyr        |
| 28 | 2,4-D | Fluroxypyr        | Penoxsulam         |
| 29 | 2,4-D | Fluroxypyr        | Pyroxsulam         |
| 30 | 2,4-D | Fluroxypyr        | Bispyribac         |
| 31 | 2,4-D | Halauxifen-methyl | Metsulfuron methyl |
| 32 | 2,4-D | Halauxifen-methyl | Bensulfuron methyl |

|    |       |                   |                    |
|----|-------|-------------------|--------------------|
| 33 | 2,4-D | Halauxifen-methyl | Pyrazosulfuron     |
| 34 | 2,4-D | Halauxifen-methyl | Imazamox           |
| 35 | 2,4-D | Halauxifen-methyl | Imazapic           |
| 36 | 2,4-D | Halauxifen-methyl | Imazapyr           |
| 37 | 2,4-D | Halauxifen-methyl | Imazethapyr        |
| 38 | 2,4-D | Halauxifen-methyl | Penoxsulam         |
| 39 | 2,4-D | Halauxifen-methyl | Pyroxsulam         |
| 40 | 2,4-D | Halauxifen-methyl | Bispyribac         |
| 41 | 2,4-D | Picloram          | Metsulfuron methyl |
| 42 | 2,4-D | Picloram          | Bensulfuron methyl |
| 43 | 2,4-D | Picloram          | Pyrazosulfuron     |
| 44 | 2,4-D | Picloram          | Imazamox           |
| 45 | 2,4-D | Picloram          | Imazapic           |
| 46 | 2,4-D | Picloram          | Imazapyr           |
| 47 | 2,4-D | Picloram          | Imazethapyr        |
| 48 | 2,4-D | Picloram          | Penoxsulam         |
| 49 | 2,4-D | Picloram          | Pyroxsulam         |
| 50 | 2,4-D | Picloram          | Bispyribac         |
| 51 | 2,4-D | Triclopyr         | Metsulfuron methyl |
| 52 | 2,4-D | Triclopyr         | Bensulfuron methyl |
| 53 | 2,4-D | Triclopyr         | Pyrazosulfuron     |
| 54 | 2,4-D | Triclopyr         | Imazamox           |
| 55 | 2,4-D | Triclopyr         | Imazapic           |
| 56 | 2,4-D | Triclopyr         | Imazapyr           |
| 57 | 2,4-D | Triclopyr         | Imazethapyr        |
| 58 | 2,4-D | Triclopyr         | Penoxsulam         |
| 59 | 2,4-D | Triclopyr         | Pyroxsulam         |
| 60 | 2,4-D | Triclopyr         | Bispyribac         |
| 61 | 2,4-D | Quinclorac        | Metsulfuron methyl |
| 62 | 2,4-D | Quinclorac        | Bensulfuron methyl |

|    |         |            |                    |
|----|---------|------------|--------------------|
| 63 | 2,4-D   | Quinclorac | Pyrazosulfuron     |
| 64 | 2,4-D   | Quinclorac | Imazamox           |
| 65 | 2,4-D   | Quinclorac | Imazapic           |
| 66 | 2,4-D   | Quinclorac | Imazapyr           |
| 67 | 2,4-D   | Quinclorac | Imazethapyr        |
| 68 | 2,4-D   | Quinclorac | Penoxsulam         |
| 69 | 2,4-D   | Quinclorac | Pyroxsulam         |
| 70 | 2,4-D   | Quinclorac | Bispyribac         |
| 71 | 2,4-D   | Quinmerac  | Metsulfuron methyl |
| 72 | 2,4-D   | Quinmerac  | Bensulfuron methyl |
| 73 | 2,4-D   | Quinmerac  | Pyrazosulfuron     |
| 74 | 2,4-D   | Quinmerac  | Imazamox           |
| 75 | 2,4-D   | Quinmerac  | Imazapic           |
| 76 | 2,4-D   | Quinmerac  | Imazapyr           |
| 77 | 2,4-D   | Quinmerac  | Imazethapyr        |
| 78 | 2,4-D   | Quinmerac  | Penoxsulam         |
| 79 | 2,4-D   | Quinmerac  | Pyroxsulam         |
| 80 | 2,4-D   | Quinmerac  | Bispyribac         |
| 81 | Dicamba | MCPA       | Metsulfuron methyl |
| 82 | Dicamba | MCPA       | Bensulfuron methyl |
| 83 | Dicamba | MCPA       | Pyrazosulfuron     |
| 84 | Dicamba | MCPA       | Imazamox           |
| 85 | Dicamba | MCPA       | Imazapic           |
| 86 | Dicamba | MCPA       | Imazapyr           |
| 87 | Dicamba | MCPA       | Imazethapyr        |
| 88 | Dicamba | MCPA       | Penoxsulam         |
| 89 | Dicamba | MCPA       | Pyroxsulam         |
| 90 | Dicamba | MCPA       | Bispyribac         |
| 91 | Dicamba | Fluroxypyr | Metsulfuron methyl |
| 92 | Dicamba | Fluroxypyr | Bensulfuron methyl |

|     |         |                   |                    |
|-----|---------|-------------------|--------------------|
| 93  | Dicamba | Fluroxypyr        | Pyrazosulfuron     |
| 94  | Dicamba | Fluroxypyr        | Imazamox           |
| 95  | Dicamba | Fluroxypyr        | Imazapic           |
| 96  | Dicamba | Fluroxypyr        | Imazapyr           |
| 97  | Dicamba | Fluroxypyr        | Imazethapyr        |
| 98  | Dicamba | Fluroxypyr        | Penoxsulam         |
| 99  | Dicamba | Fluroxypyr        | Pyroxsulam         |
| 100 | Dicamba | Fluroxypyr        | Bispyribac         |
| 101 | Dicamba | Halauxifen-methyl | Metsulfuron methyl |
| 102 | Dicamba | Halauxifen-methyl | Bensulfuron methyl |
| 103 | Dicamba | Halauxifen-methyl | Pyrazosulfuron     |
| 104 | Dicamba | Halauxifen-methyl | Imazamox           |
| 105 | Dicamba | Halauxifen-methyl | Imazapic           |
| 106 | Dicamba | Halauxifen-methyl | Imazapyr           |
| 107 | Dicamba | Halauxifen-methyl | Imazethapyr        |
| 108 | Dicamba | Halauxifen-methyl | Penoxsulam         |
| 109 | Dicamba | Halauxifen-methyl | Pyroxsulam         |
| 110 | Dicamba | Halauxifen-methyl | Bispyribac         |
| 111 | Dicamba | Picloram          | Metsulfuron methyl |
| 112 | Dicamba | Picloram          | Bensulfuron methyl |
| 113 | Dicamba | Picloram          | Pyrazosulfuron     |
| 114 | Dicamba | Picloram          | Imazamox           |
| 115 | Dicamba | Picloram          | Imazapic           |
| 116 | Dicamba | Picloram          | Imazapyr           |
| 117 | Dicamba | Picloram          | Imazethapyr        |
| 118 | Dicamba | Picloram          | Penoxsulam         |
| 119 | Dicamba | Picloram          | Pyroxsulam         |
| 120 | Dicamba | Picloram          | Bispyribac         |
| 121 | Dicamba | Triclopyr         | Metsulfuron methyl |
| 122 | Dicamba | Triclopyr         | Bensulfuron methyl |

|     |         |            |                    |
|-----|---------|------------|--------------------|
| 123 | Dicamba | Triclopyr  | Pyrazosulfuron     |
| 124 | Dicamba | Triclopyr  | Imazamox           |
| 125 | Dicamba | Triclopyr  | Imazapic           |
| 126 | Dicamba | Triclopyr  | Imazapyr           |
| 127 | Dicamba | Triclopyr  | Imazethapyr        |
| 128 | Dicamba | Triclopyr  | Penoxsulam         |
| 129 | Dicamba | Triclopyr  | Pyroxsulam         |
| 130 | Dicamba | Triclopyr  | Bispyribac         |
| 131 | Dicamba | Quinclorac | Metsulfuron methyl |
| 132 | Dicamba | Quinclorac | Bensulfuron methyl |
| 133 | Dicamba | Quinclorac | Pyrazosulfuron     |
| 134 | Dicamba | Quinclorac | Imazamox           |
| 135 | Dicamba | Quinclorac | Imazapic           |
| 136 | Dicamba | Quinclorac | Imazapyr           |
| 137 | Dicamba | Quinclorac | Imazethapyr        |
| 138 | Dicamba | Quinclorac | Penoxsulam         |
| 139 | Dicamba | Quinclorac | Pyroxsulam         |
| 140 | Dicamba | Quinclorac | Bispyribac         |
| 141 | Dicamba | Quinmerac  | Metsulfuron methyl |
| 142 | Dicamba | Quinmerac  | Bensulfuron methyl |
| 143 | Dicamba | Quinmerac  | Pyrazosulfuron     |
| 144 | Dicamba | Quinmerac  | Imazamox           |
| 145 | Dicamba | Quinmerac  | Imazapic           |
| 146 | Dicamba | Quinmerac  | Imazapyr           |
| 147 | Dicamba | Quinmerac  | Imazethapyr        |
| 148 | Dicamba | Quinmerac  | Penoxsulam         |
| 149 | Dicamba | Quinmerac  | Pyroxsulam         |
| 150 | Dicamba | Quinmerac  | Bispyribac         |
| 151 | MCPA    | Dicamba    | Metsulfuron methyl |
| 152 | MCPA    | Dicamba    | Bensulfuron methyl |

|     |      |                   |                    |
|-----|------|-------------------|--------------------|
| 153 | MCPA | Dicamba           | Pyrazosulfuron     |
| 154 | MCPA | Dicamba           | Imazamox           |
| 155 | MCPA | Dicamba           | Imazapic           |
| 156 | MCPA | Dicamba           | Imazapyr           |
| 157 | MCPA | Dicamba           | Imazethapyr        |
| 158 | MCPA | Dicamba           | Penoxsulam         |
| 159 | MCPA | Dicamba           | Pyroxsulam         |
| 160 | MCPA | Dicamba           | Bispyribac         |
| 161 | MCPA | Fluroxypyr        | Metsulfuron methyl |
| 162 | MCPA | Fluroxypyr        | Bensulfuron methyl |
| 163 | MCPA | Fluroxypyr        | Pyrazosulfuron     |
| 164 | MCPA | Fluroxypyr        | Imazamox           |
| 165 | MCPA | Fluroxypyr        | Imazapic           |
| 166 | MCPA | Fluroxypyr        | Imazapyr           |
| 167 | MCPA | Fluroxypyr        | Imazethapyr        |
| 168 | MCPA | Fluroxypyr        | Penoxsulam         |
| 169 | MCPA | Fluroxypyr        | Pyroxsulam         |
| 170 | MCPA | Fluroxypyr        | Bispyribac         |
| 171 | MCPA | Halauxifen-methyl | Metsulfuron methyl |
| 172 | MCPA | Halauxifen-methyl | Bensulfuron methyl |
| 173 | MCPA | Halauxifen-methyl | Pyrazosulfuron     |
| 174 | MCPA | Halauxifen-methyl | Imazamox           |
| 175 | MCPA | Halauxifen-methyl | Imazapic           |
| 176 | MCPA | Halauxifen-methyl | Imazapyr           |
| 177 | MCPA | Halauxifen-methyl | Imazethapyr        |
| 178 | MCPA | Halauxifen-methyl | Penoxsulam         |
| 179 | MCPA | Halauxifen-methyl | Pyroxsulam         |
| 180 | MCPA | Halauxifen-methyl | Bispyribac         |
| 181 | MCPA | Picloram          | Metsulfuron methyl |
| 182 | MCPA | Picloram          | Bensulfuron methyl |

|     |      |            |                    |
|-----|------|------------|--------------------|
| 183 | MCPA | Picloram   | Pyrazosulfuron     |
| 184 | MCPA | Picloram   | Imazamox           |
| 185 | MCPA | Picloram   | Imazapic           |
| 186 | MCPA | Picloram   | Imazapyr           |
| 187 | MCPA | Picloram   | Imazethapyr        |
| 188 | MCPA | Picloram   | Penoxsulam         |
| 189 | MCPA | Picloram   | Pyroxsulam         |
| 190 | MCPA | Picloram   | Bispyribac         |
| 191 | MCPA | Triclopyr  | Metsulfuron methyl |
| 192 | MCPA | Triclopyr  | Bensulfuron methyl |
| 193 | MCPA | Triclopyr  | Pyrazosulfuron     |
| 194 | MCPA | Triclopyr  | Imazamox           |
| 195 | MCPA | Triclopyr  | Imazapic           |
| 196 | MCPA | Triclopyr  | Imazapyr           |
| 197 | MCPA | Triclopyr  | Imazethapyr        |
| 198 | MCPA | Triclopyr  | Penoxsulam         |
| 199 | MCPA | Triclopyr  | Pyroxsulam         |
| 200 | MCPA | Triclopyr  | Bispyribac         |
| 201 | MCPA | Quinclorac | Metsulfuron methyl |
| 202 | MCPA | Quinclorac | Bensulfuron methyl |
| 203 | MCPA | Quinclorac | Pyrazosulfuron     |
| 204 | MCPA | Quinclorac | Imazamox           |
| 205 | MCPA | Quinclorac | Imazapic           |
| 206 | MCPA | Quinclorac | Imazapyr           |
| 207 | MCPA | Quinclorac | Imazethapyr        |
| 208 | MCPA | Quinclorac | Penoxsulam         |
| 209 | MCPA | Quinclorac | Pyroxsulam         |
| 210 | MCPA | Quinclorac | Bispyribac         |
| 211 | MCPA | Quinmerac  | Metsulfuron methyl |
| 212 | MCPA | Quinmerac  | Bensulfuron methyl |

|     |            |                   |                    |
|-----|------------|-------------------|--------------------|
| 213 | MCPA       | Quinmerac         | Pyrazosulfuron     |
| 214 | MCPA       | Quinmerac         | Imazamox           |
| 215 | MCPA       | Quinmerac         | Imazapic           |
| 216 | MCPA       | Quinmerac         | Imazapyr           |
| 217 | MCPA       | Quinmerac         | Imazethapyr        |
| 218 | MCPA       | Quinmerac         | Penoxsulam         |
| 219 | MCPA       | Quinmerac         | Pyroxsulam         |
| 220 | MCPA       | Quinmerac         | Bispyribac         |
| 221 | Fluroxypyr | Halauxifen-methyl | Metsulfuron methyl |
| 222 | Fluroxypyr | Halauxifen-methyl | Bensulfuron methyl |
| 223 | Fluroxypyr | Halauxifen-methyl | Pyrazosulfuron     |
| 224 | Fluroxypyr | Halauxifen-methyl | Imazamox           |
| 225 | Fluroxypyr | Halauxifen-methyl | Imazapic           |
| 226 | Fluroxypyr | Halauxifen-methyl | Imazapyr           |
| 227 | Fluroxypyr | Halauxifen-methyl | Imazethapyr        |
| 228 | Fluroxypyr | Halauxifen-methyl | Penoxsulam         |
| 229 | Fluroxypyr | Halauxifen-methyl | Pyroxsulam         |
| 230 | Fluroxypyr | Halauxifen-methyl | Bispyribac         |
| 231 | Fluroxypyr | Picloram          | Metsulfuron methyl |
| 232 | Fluroxypyr | Picloram          | Bensulfuron methyl |
| 233 | Fluroxypyr | Picloram          | Pyrazosulfuron     |
| 234 | Fluroxypyr | Picloram          | Imazamox           |
| 235 | Fluroxypyr | Picloram          | Imazapic           |
| 236 | Fluroxypyr | Picloram          | Imazapyr           |
| 237 | Fluroxypyr | Picloram          | Imazethapyr        |
| 238 | Fluroxypyr | Picloram          | Penoxsulam         |
| 239 | Fluroxypyr | Picloram          | Pyroxsulam         |
| 240 | Fluroxypyr | Picloram          | Bispyribac         |
| 241 | Fluroxypyr | Triclopyr         | Metsulfuron methyl |
| 242 | Fluroxypyr | Triclopyr         | Bensulfuron methyl |

|     |                  |            |                    |
|-----|------------------|------------|--------------------|
| 243 | Fluroxypyr       | Triclopyr  | Pyrazosulfuron     |
| 244 | Fluroxypyr       | Triclopyr  | Imazamox           |
| 245 | Fluroxypyr       | Triclopyr  | Imazapic           |
| 246 | Fluroxypyr       | Triclopyr  | Imazapyr           |
| 247 | Fluroxypyr       | Triclopyr  | Imazethapyr        |
| 248 | Fluroxypyr       | Triclopyr  | Penoxsulam         |
| 249 | Fluroxypyr       | Triclopyr  | Pyroxsulam         |
| 250 | Fluroxypyr       | Triclopyr  | Bispyribac         |
| 251 | Fluroxypyr       | Quinclorac | Metsulfuron methyl |
| 252 | Fluroxypyr       | Quinclorac | Bensulfuron methyl |
| 253 | Fluroxypyr       | Quinclorac | Pyrazosulfuron     |
| 254 | Fluroxypyr       | Quinclorac | Imazamox           |
| 255 | Fluroxypyr       | Quinclorac | Imazapic           |
| 256 | Fluroxypyr       | Quinclorac | Imazapyr           |
| 257 | Fluroxypyr       | Quinclorac | Imazethapyr        |
| 258 | Fluroxypyr       | Quinclorac | Penoxsulam         |
| 259 | Fluroxypyr       | Quinclorac | Pyroxsulam         |
| 260 | Fluroxypyr       | Quinclorac | Bispyribac         |
| 261 | Fluroxypyr       | Quinmerac  | Metsulfuron methyl |
| 262 | Fluroxypyr       | Quinmerac  | Bensulfuron methyl |
| 263 | Fluroxypyr       | Quinmerac  | Pyrazosulfuron     |
| 264 | Fluroxypyr       | Quinmerac  | Imazamox           |
| 265 | Fluroxypyr       | Quinmerac  | Imazapic           |
| 266 | Fluroxypyr       | Quinmerac  | Imazapyr           |
| 267 | Fluroxypyr       | Quinmerac  | Imazethapyr        |
| 268 | Fluroxypyr       | Quinmerac  | Penoxsulam         |
| 269 | Fluroxypyr       | Quinmerac  | Pyroxsulam         |
| 270 | Fluroxypyr       | Quinmerac  | Bispyribac         |
| 271 | Halaxifen-methyl | Picloram   | Metsulfuron methyl |

|     |                   |           |                    |
|-----|-------------------|-----------|--------------------|
| 272 | Halauxifen-methyl | Picloram  | Bensulfuron methyl |
| 273 | Halauxifen-methyl | Picloram  | Pyrazosulfuron     |
| 274 | Halauxifen-methyl | Picloram  | Imazamox           |
| 275 | Halauxifen-methyl | Picloram  | Imazapic           |
| 276 | Halauxifen-methyl | Picloram  | Imazapyr           |
| 277 | Halauxifen-methyl | Picloram  | Imazethapyr        |
| 278 | Halauxifen-methyl | Picloram  | Penoxsulam         |
| 279 | Halauxifen-methyl | Picloram  | Pyroxsulam         |
| 280 | Halauxifen-methyl | Picloram  | Bispyribac         |
| 281 | Halauxifen-methyl | Triclopyr | Metsulfuron methyl |
| 282 | Halauxifen-methyl | Triclopyr | Bensulfuron methyl |
| 283 | Halauxifen-methyl | Triclopyr | Pyrazosulfuron     |
| 284 | Halauxifen-methyl | Triclopyr | Imazamox           |
| 285 | Halauxifen-methyl | Triclopyr | Imazapic           |
| 286 | Halauxifen-methyl | Triclopyr | Imazapyr           |

|     |                   |            |                    |
|-----|-------------------|------------|--------------------|
| 287 | Halauxifen-methyl | Triclopyr  | Imazethapyr        |
| 288 | Halauxifen-methyl | Triclopyr  | Penoxsulam         |
| 289 | Halauxifen-methyl | Triclopyr  | Pyroxsulam         |
| 290 | Halauxifen-methyl | Triclopyr  | Bispyribac         |
| 291 | Halauxifen-methyl | Quinclorac | Metsulfuron methyl |
| 292 | Halauxifen-methyl | Quinclorac | Bensulfuron methyl |
| 293 | Halauxifen-methyl | Quinclorac | Pyrazosulfuron     |
| 294 | Halauxifen-methyl | Quinclorac | Imazamox           |
| 295 | Halauxifen-methyl | Quinclorac | Imazapic           |
| 296 | Halauxifen-methyl | Quinclorac | Imazapyr           |
| 297 | Halauxifen-methyl | Quinclorac | Imazethapyr        |
| 298 | Halauxifen-methyl | Quinclorac | Penoxsulam         |
| 299 | Halauxifen-methyl | Quinclorac | Pyroxsulam         |
| 300 | Halauxifen-methyl | Quinclorac | Bispyribac         |
| 301 | Halauxifen-methyl | Quinmerac  | Metsulfuron methyl |

|     |                   |            |                    |
|-----|-------------------|------------|--------------------|
| 302 | Halauxifen-methyl | Quinmerac  | Bensulfuron methyl |
| 303 | Halauxifen-methyl | Quinmerac  | Pyrazosulfuron     |
| 304 | Halauxifen-methyl | Quinmerac  | Imazamox           |
| 305 | Halauxifen-methyl | Quinmerac  | Imazapic           |
| 306 | Halauxifen-methyl | Quinmerac  | Imazapyr           |
| 307 | Halauxifen-methyl | Quinmerac  | Imazethapyr        |
| 308 | Halauxifen-methyl | Quinmerac  | Penoxsulam         |
| 309 | Halauxifen-methyl | Quinmerac  | Pyroxsulam         |
| 310 | Halauxifen-methyl | Quinmerac  | Bispyribac         |
| 311 | Picloram          | Triclopyr  | Metsulfuron methyl |
| 312 | Picloram          | Triclopyr  | Bensulfuron methyl |
| 313 | Picloram          | Triclopyr  | Pyrazosulfuron     |
| 314 | Picloram          | Triclopyr  | Imazamox           |
| 315 | Picloram          | Triclopyr  | Imazapic           |
| 316 | Picloram          | Triclopyr  | Imazapyr           |
| 317 | Picloram          | Triclopyr  | Imazethapyr        |
| 318 | Picloram          | Triclopyr  | Penoxsulam         |
| 319 | Picloram          | Triclopyr  | Pyroxsulam         |
| 320 | Picloram          | Triclopyr  | Bispyribac         |
| 321 | Picloram          | Quinclorac | Metsulfuron methyl |
| 322 | Picloram          | Quinclorac | Bensulfuron methyl |
| 323 | Picloram          | Quinclorac | Pyrazosulfuron     |

|     |           |            |                    |
|-----|-----------|------------|--------------------|
| 324 | Picloram  | Quinclorac | Imazamox           |
| 325 | Picloram  | Quinclorac | Imazapic           |
| 326 | Picloram  | Quinclorac | Imazapyr           |
| 327 | Picloram  | Quinclorac | Imazethapyr        |
| 328 | Picloram  | Quinclorac | Penoxsulam         |
| 329 | Picloram  | Quinclorac | Pyroxsulam         |
| 330 | Picloram  | Quinclorac | Bispyribac         |
| 331 | Picloram  | Quinmerac  | Metsulfuron methyl |
| 332 | Picloram  | Quinmerac  | Bensulfuron methyl |
| 333 | Picloram  | Quinmerac  | Pyrazosulfuron     |
| 334 | Picloram  | Quinmerac  | Imazamox           |
| 335 | Picloram  | Quinmerac  | Imazapic           |
| 336 | Picloram  | Quinmerac  | Imazapyr           |
| 337 | Picloram  | Quinmerac  | Imazethapyr        |
| 338 | Picloram  | Quinmerac  | Penoxsulam         |
| 339 | Picloram  | Quinmerac  | Pyroxsulam         |
| 340 | Picloram  | Quinmerac  | Bispyribac         |
| 341 | Triclopyr | Quinclorac | Metsulfuron methyl |
| 342 | Triclopyr | Quinclorac | Bensulfuron methyl |
| 343 | Triclopyr | Quinclorac | Pyrazosulfuron     |
| 344 | Triclopyr | Quinclorac | Imazamox           |
| 345 | Triclopyr | Quinclorac | Imazapic           |
| 346 | Triclopyr | Quinclorac | Imazapyr           |
| 347 | Triclopyr | Quinclorac | Imazethapyr        |
| 348 | Triclopyr | Quinclorac | Penoxsulam         |
| 349 | Triclopyr | Quinclorac | Pyroxsulam         |
| 350 | Triclopyr | Quinclorac | Bispyribac         |
| 351 | Triclopyr | Quinmerac  | Metsulfuron methyl |
| 352 | Triclopyr | Quinmerac  | Bensulfuron methyl |
| 353 | Triclopyr | Quinmerac  | Pyrazosulfuron     |

|     |            |           |                    |
|-----|------------|-----------|--------------------|
| 354 | Triclopyr  | Quinmerac | Imazamox           |
| 355 | Triclopyr  | Quinmerac | Imazapic           |
| 356 | Triclopyr  | Quinmerac | Imazapyr           |
| 357 | Triclopyr  | Quinmerac | Imazethapyr        |
| 358 | Triclopyr  | Quinmerac | Penoxsulam         |
| 359 | Triclopyr  | Quinmerac | Pyroxsulam         |
| 360 | Triclopyr  | Quinmerac | Bispyribac         |
| 361 | Quinclorac | Quinmerac | Metsulfuron methyl |
| 362 | Quinclorac | Quinmerac | Bensulfuron methyl |
| 363 | Quinclorac | Quinmerac | Pyrazosulfuron     |
| 364 | Quinclorac | Quinmerac | Imazamox           |
| 365 | Quinclorac | Quinmerac | Imazapic           |
| 366 | Quinclorac | Quinmerac | Imazapyr           |
| 367 | Quinclorac | Quinmerac | Imazethapyr        |
| 368 | Quinclorac | Quinmerac | Penoxsulam         |
| 369 | Quinclorac | Quinmerac | Pyroxsulam         |
| 370 | Quinclorac | Quinmerac | Bispyribac         |

In an embodiment, the present invention may provide a combination comprising the three herbicides as listed in each individual row from row 1 to row 370 in the table above.

5

Another aspect of the present invention may provide a composition.

In an embodiment, the composition may comprise the combination comprising the three herbicides as listed in each individual row from row 1 to row 370 in the table  
10 above along with an agrochemically acceptable excipient.

Thus, an embodiment of the present invention may provide a composition comprising:

(a) picloram;

- (b) 2,4D;
- (c) metsulfuron methyl; and
- (d) agrochemically acceptable adjuvants.

5 The combination may be applied to the locus of the weeds in an herbicidally effective amount. The selection of the appropriate effective amounts depends on the density of weed infestation, weather patterns, crop health and many other factors, which may be made conveniently by a person skilled in the art. The effective amounts of these herbicides in the synergistic combination of the present  
10 invention is not particularly limiting.

In an embodiment, the combination of the present invention may be combined with at least one other active ingredient selected from the group consisting of herbicides, insecticides, fungicides, biological agents, plant growth activators,  
15 fertilizers or combinations thereof.

Thus, in an embodiment, the combination of the present invention may be combined with another herbicide. Exemplary herbicides that may be combined with the combination of the present invention may be selected from, but not limited to,  
20 herbicides belonging to classes such as ACCase inhibitors, EPSP synthase inhibitors, auxin transport inhibitors, glutamate synthase inhibitors, HPPD inhibitors, lipid synthesis inhibitors, long chain fatty acid inhibitors, as well as herbicides with unknown modes of action.

25 In an embodiment, the total amount of synthetic auxins in the composition may typically be in the range of 0.1 to 99% by weight, preferably 0.2 to 90% by weight. The total amount of sulfonylurea herbicide in the composition may be in the range of 0.1 to 99% by weight.

30 In an embodiment, the constituent herbicides of the combination of the present invention may be admixed in ratio of (1-80): (1-80): (1-80) of first synthetic auxin, second synthetic auxin, and sulfonylurea herbicide respectively. Preferably, the

ratio of the constituents of the present invention may be admixed in the ratio of (1-50): (1-50): (1-50) of first synthetic, auxin second synthetic auxin, and sulfonylurea herbicide respectively.

- 5 In an embodiment, it was found that the precise ratio or quantities of the herbicides in the present invention was not particularly critical to achieve the synergistic effect as long as the selective herbicides were used at their recommended dosage levels. These recommended dosage levels of the herbicides of the invention are known and do not form a critical part of the instant invention although their selection is  
10 important to achieve the desired synergistic effect.

The herbicidal combination of the present invention maybe used to target weeds among the crops such corn, rice, wheat, barley, rye, oat, sorghum, cotton, soybean, peanut, buckwheat, beet, rapeseed, sunflower, sugar cane, tobacco,  
15 etc.; vegetables: solanaceous vegetables such as eggplant, tomato, pimento, pepper, potato, etc., cucurbit vegetables such as cucumber, pumpkin, zucchini, water melon, melon, squash, etc., cruciferous vegetables such as radish, white turnip, horseradish, kohlrabi, Chinese cabbage, cabbage, leaf mustard, broccoli, cauliflower, etc., asteraceous vegetables such as burdock, crown daisy, artichoke,  
20 lettuce, etc, liliaceous vegetables such as green onion, onion, garlic, and asparagus, ammiaceous vegetables such as carrot, parsley, celery, parsnip, etc., chenopodiaceous vegetables such as spinach, Swiss chard, etc., lamiaceous vegetables such as Perilla frutescens, mint, basil, etc, strawberry, sweet potato, Dioscorea japonica, colocasia, etc., flowers, foliage plants, turf grasses, pastures,  
25 fruits: pome fruits such apple, pear, quince, etc, stone fleshy fruits such as peach, plum, nectarine, Prunus mume, cherry fruit, apricot, prune, etc., citrus fruits such as orange, lemon, lime, grapefruit, etc., nuts such as chestnuts, walnuts, hazelnuts, almond, pistachio, cashew nuts, macadamia nuts, etc. berries such as blueberry, cranberry, blackberry, raspberry, etc., vines, kaki fruit, olive, plum,  
30 banana, oil palm, coffee, date palm, coconuts, etc. , trees other than fruit trees; tea, mulberry, flowering plant, trees such as ash, birch, dogwood, Eucalyptus, Ginkgo biloba, lilac, maple, Quercus, poplar, Judas tree, Liquidambar formosana, plane

## 25

tree, zelkova, Japanese arborvitae, fir wood, hemlock, juniper, Pinus, Picea, and Taxus cuspidate, etc.

Thus, in another aspect, the present invention provides a method of controlling weeds at a locus, the method comprising applying a combination comprising at least two synthetic auxins and a sulfonyleurea herbicide to the locus.

In an embodiment, the present invention provides a method of controlling weeds at a locus, the method comprising applying a combination comprising at least two synthetic auxins and at least one ALS inhibitor to the locus.

Thus, embodiments of the present invention may provide a method of controlling weeds at a locus, said method comprising application of synergistic combination of picloram; 2,4-D; and metsulfuron methyl.

Thus, embodiments of the present invention may provide a method of controlling weeds at a locus, said method comprising application of synergistic combination of picloram; 2,4-D; metsulfuron methyl, and a fourth active ingredient.

In an embodiment, the fourth active ingredient may selected from herbicide, insecticide, fungicide, biological agent, plant growth activator, fertilizers and combinations thereof.

The target weeds may be selected from Urticaceae weeds: *Urtica urens*;  
Polygonaceae weeds: *Polygonum convolvulus*, *Polygonum lapathifolium*, *Polygonum pensylvanicum*, *Polygonum persicaria*, *Polygonum longisetum*, *Polygonum aviculare*, *Polygonum arenastrum*, *Polygonum cuspidatum*, *Rumex japonicus*, *Rumex crispus*, *Rumex obtusifolius*, *Rumex acetosa*; Portulacaceae weeds: *Portulaca oleracea*; Caryophyllaceae weeds: *Stellaria media*, *Cerastium holosteoides*, *Cerastium glomeratum*, *Spergula arvensis*, *Silene gallica*;  
Molluginaceae weeds: *Mollugo verticillata*; Chenopodiaceae weeds: *Chenopodium album*, *Chenopodium ambrosioides*, *Kochia scoparia*, *Salsola kali*, *Atriplex* spp.;

## 26

Amaranthaceae weeds: *Amaranthus retroflexus*, *Amaranthus viridis*, *Amaranthus lividus*, *Amaranthus spinosus*, *Amaranthus hybridus*, *Amaranthus palmeri*, *Amaranthus rudis*, *Amaranthus patulus*, *Amaranthus tuberculatus*, *Amaranthus blitoides*, *Amaranthus deflexus*, *Amaranthus quitensis*, *Alternanthera philoxeroides*, *Alternanthera sessilis*, *Alternanthera tenella*; Papaveraceae weeds: *Papaver rhoeas*, *Argemone Mexicana*; Brassicaceae weeds: *Raphanus raphanistrum*, *Raphanus sativus*, *Sinapis arvensis*, *Capsella bursa-pastoris*, *Brassica juncea*, *Brassica campestris*, *Descurainia pinnata*, *Rorippa islandica*, *Rorippa sylvestris*, *Thlaspi arvense*, *Myagrum rugosum*, *Lepidium virginicum*, *Coronopus didymus*; Capparaceae weeds: *Cleome affinis*; Fabaceae weeds: *Aeschynomene indica*, *Aeschynomene rudis*, *Sesbania exaltata*, *Cassia obtusifolia*, *Cassia occidentalis*, *Desmodium tortuosum*, *Desmodium adscendens*, *Trifolium repens*, *Pueraria lobata*, *Vicia angustifolia*, *Indigofera hirsuta*, *Indigofera truxillensis*, *Vigna sinensis*; Oxalidaceae weeds: *Oxalis corniculata*, *Oxalis stricta*, *Oxalis oxyptera*; Geraniaceae weeds: *Geranium carolinense*, *Erodium cicutarium*; Euphorbiaceae weeds: *Euphorbia helioscopia*, *Euphorbia maculata*, *Euphorbia humistrata*, *Euphorbia esula*, *Euphorbia heterophylla*, *Euphorbia brasiliensis*, *Acalypha australis*, *Croton glandulosus*, *Croton lobatus*, *Phyllanthus corcovadensis*, *Ricinus communis*; Malvaceae weeds: *Abutilon theophrasti*, *Sida rhombifolia*, *Sida cordifolia*, *Sida spinosa*, *Sida glaziovii*, *Sida santaremnensis*, *Hibiscus trionum*, *Anoda cristata*, *Malvastrum coromandelianum*; Sterculiaceae weeds: *Waltheria indica*; Violaceae weeds: *Viola arvensis*, *Viola tricolor*; Cucurbitaceae weeds: *Sicyos angulatus*, *Echinocystis lobata*, *Momordica charantia*; Lythraceae weeds: *Lythrum salicaria*; Apiaceae weeds: *Hydrocotyle sibthorpioides*; Sapindaceae weeds: *Cardiospermum halicacabum*; Primulaceae weeds: *Anagallis arvensis*; Asclepiadaceae weeds: *Asclepias syriaca*, *Ampelamus albidus*; Rubiaceae weeds: *Galium aparine*, *Galium spurium* var. *echinospermon*, *Spermacoce latifolia*, *Richardia brasiliensis*, *Borreria alata*; Convolvulaceae weeds: *Ipomoea nil*, *Ipomoea hederacea*, *Ipomoea purpurea*, *Ipomoea hederacea* var. *integriuscula*, *Ipomoea lacunosa*, *Ipomoea triloba*, *Ipomoea acuminata*, *Ipomoea hederifolia*, *Ipomoea coccinea*, *Ipomoea quamoclit*, *Ipomoea grandifolia*, *Ipomoea aristolochiaefolia*, *Ipomoea cairica*, *Convolvulus arvensis*, *Calystegia*

hederacea, *Calystegia japonica*, *Merremia hedeacea*, *Merremia aegyptia*,  
*Merremia cissoides*, *Jacquemontia tamnifolia*; Boraginaceae weeds: *Myosotis*  
*arvensis*; Lamiaceae weeds: *Lamium purpureum*, *Lamium amplexicaule*, *Leonotis*  
*nepetaefolia*, *Hyptis suaveolens*, *Hyptis lophanta*, *Leonurus sibiricus*, *Stachys*  
 5 *arvensis*; Solanaceae weeds: *Datura stramonium*, *Solanum nigrum*, *Solanum*  
*americanum*, *Solanum ptycanthum*, *Solanum sarrachoides*, *Solanum rostratum*,  
*Solanum aculeatissimum*, *Solanum sisymbriifolium*, *Solanum carolinense*,  
*Physalis angulata*, *Physalis subglabrata*, *Nicandra physaloides*; Scrophulariaceae  
 weeds: *Veronica hederæfolia*, *Veronica persica*, *Veronica arvensis*;  
 10 Plantaginaceae weeds: *Plantago asiatica*; Asteraceae weeds: *Xanthium*  
*pensylvanicum*, *Xanthium occidentale*, *Helianthus annuus*, *Matricaria chamomilla*,  
*Matricaria perforata*, *Chrysanthemum segetum*, *Matricaria matricarioides*,  
*Artemisia princeps*, *Artemisia vulgaris*, *Artemisia verlotorum*, *solidago altissima*,  
*Taraxacum officinale*, *Galinsoga ciliata*, *Galinsoga parviflora*, *Senecio vulgaris*,  
 15 *Senecio brasiliensis*, *Senecio grisebachii*, *Conyza bonariensis*, *Conyza*  
*canadensis*, *Ambrosia artemisiaefolia*, *Ambrosia trifida*, *Bidens pilosa*, *Bidens*  
*frondosa*, *Bidens subalternans*, *Cirsium arvense*, *Cirsium vulgare*, *Silybum*  
*marianum*, *Carduus nutans*, *Lactuca serriola*, *Sonchus oleraceus*, *Sonchus asper*,  
*Wedelia glauca*, *Melampodium perfoliatum*, *Emilia sonchifolia*, *Tagetes minuta*,  
 20 *Blainvillea latifolia*, *Tridax procumbens*, *Porophyllum ruderale*, *Acanthospermum*  
*australe*, *Acanthospermum hispidum*, *Cardiospermum halicacabum*, *Ageratum*  
*conyzoides*, *Eupatorium perfoliatum*, *Eclipta alba*, *Erechtites hieracifolia*,  
*Gamochaeta spicata*, *Gnaphalium spicatum*, *Jaegeria hirta*, *Parthenium*  
*hysterophorus*, *Siegesbeckia orientalis*, *Soliva sessilis*; Liliaceae weeds: *Allium*  
 25 *canadense*, *Allium vineale*; Commelinaceae weeds: *Commelina communis*,  
*Commelina bengharensis*, *Commelina erecta*; Poaceae weeds: *Echinochloa crus-*  
*galli*, *Setaria viridis*, *Setaria faberi*, *Setaria glauca*, *Setaria geniculata*, *Digitaria*  
*ciliaris*, *Digitaria sanguinalis*, *Digitaria horizontalis*, *Digitaria insularis*, *Eleusine*  
*indica*, *Poa annua*, *Alopecurus aequalis*, *Alopecurus myosuroides*, *Avena fatua*,  
 30 *Sorghum halepense*, *Sorghum vulgare*, *Agropyron repens*, *Lolium multiflorum*,  
*Lolium perenne*, *Lolium rigidum*, *Bromus secalinus*, *Bromus tectorum*, *Hordeum*  
*jubatum*, *Aegilops cylindrica*, *Phalaris arundinacea*, *Phalaris minor*, *Apera spica-*

venti, *Panicum dichotomiflorum*, *Panicum texanum*, *Panicum maximum*, *Brachiaria platyphylla*, *Brachiaria ruziziensis*, *Brachiaria plantaginea*, *Brachiaria decumbens*, *Brachiaria brizantha*, *Brachiaria humidicola*, *Cenchrus echinatus*, *Cenchrus pauciflorus*, *Eriochloa villosa*, *Pennisetum setosum*, *Chloris gayana*, *Eragrostis pilosa*, *Rhynchelitrum repens*, *Dactyloctenium aegyptium*, *Ischaemum rugosum*,  
5 *Oryza sativa*, *Paspalum notatum*, *Paspalum maritimum*, *Pennisetum clandestinum*, *Pennisetum setosum*, *Rottboellia cochinchinensis*; Cyperaceae weeds: *Cyperus microiria*, *Cyperus iria*, *Cyperus odoratus*, *Cyperus rotundus*, *Cyperus esculentus*, *Kyllinga gracillima*  
10 Equisetaceae weeds: *Equisetum arvense*, *Equisetum palustre*, and the like.

In an embodiment, the individual components of the combination of the present invention may be applied to the locus either simultaneously or sequentially, such that at least two auxins and at least one sulfonylurea herbicide may be applied in  
15 a tank mix or as a pre-mixed composition.

In an embodiment, combination of the present invention may be applied either pre or post emergent. The advantage of the combination is surprisingly good residual effects, when applied in pre-emergent as well as quick knockdown when applied  
20 post emergent leading to quick control of weeds.

The method of control of the present invention may be carried out by spraying the suggested tank mixes, or the individual herbicides may be formulated as a kit-of-parts containing various components that may be mixed as instructed prior to  
25 spraying.

In an embodiment the components of the present invention may be packaged such that at least two auxins and at least one sulfonylurea herbicide may be packaged separately and then tank mixed before the spraying.  
30

In another embodiment the components of the present invention may be packaged such that picloram, 2,4-D and metsulfuron methyl may be packaged separately,

whereas other additives are packaged separately, such that the two maybe tank mixed at the time of spraying.

In another embodiment the components of the present invention may be packaged  
5 as composition such that at least two synthetic auxin herbicide and at least one  
sulfonylurea herbicide may be formulated into one composition and other additives  
are packaged separately, such that the two maybe tank mixed at the time of  
spraying.

10 Therefore, in another aspect, the present invention may provide compositions  
comprising at least two synthetic auxin herbicides, at least one sulfonylurea  
herbicide and at least one agrochemically acceptable excipient.

In an embodiment, the present invention may provide compositions comprising  
15 picloram and 2,4-D and metsulfuron methyl.

In an embodiment, the composition of the present invention may contain  
agriculturally acceptable adjuvants, carriers, diluents, emulsifiers, fillers, anti-  
foaming agents, thickening agents, anti-freezing agents, freezing agents etc. The  
20 compositions may be either solid or liquids. They can be solids, such as, for  
example, dusts, granules, water-dispersible granules, microcapsules or wettable  
powders, or liquids, such as, for example, emulsifiable concentrates, solutions,  
emulsions or suspensions, ZC formulations. They can also be provided as a pre-  
mix or tank mixes.

25

Suitable agricultural adjuvants and carriers may include, but are not limited to, crop  
oil concentrates; methylated seed oils, emulsified methylated seed oil, nonylphenol  
ethoxylate; benzylcocoalkyldimethyl quaternary ammonium salt; blend of  
petroleum hydrocarbon, alkyl esters, organic acid, and anionic surfactant; C<sub>9</sub>-C<sub>11</sub>  
30 alkylpolyglycoside; phosphated alcohol ethoxylate; natural primary alcohol (C<sub>12</sub>-  
C<sub>16</sub>) ethoxylate; di-sec-butylphenol EO-PO block copolymer; polysiloxane-methyl  
cap; nonylphenol ethoxylate, urea ammonium nitrate; tridecyl alcohol (synthetic)

ethoxylate (8EO); tallow amine ethoxylate ; PEG(400) dioleate-99, alkyl sulfates, such as diethanolammonium lauryl sulfate; alkylarylsulfonate salts, such as calcium dodecylbenzenesulfonate; alkylphenol-alkylene oxide addition products, such as nonylphenol-C<sub>18</sub>ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol-C<sub>16</sub> ethoxylate; soaps, such as sodium stearate; alkyl-naphthalene-sulfonate salts, such as sodium dibutyl-naphthalenesulfonate; 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; salts of mono and dialkyl phosphate esters; vegetable or seed oils such as soybean oil, rapeseed/canola oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; and esters of the above vegetable oils, , methyl esters and the like.

Suitable liquid carriers that may be employed in a composition of the present invention may include water or organic solvents. The organic solvents include, but are not limited to, petroleum fractions or hydrocarbons such as mineral oil, aromatic solvents, paraffinic oils, and the like; vegetable oils such as soybean oil, rapeseed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; esters of the above vegetable oils; esters of monoalcohols or dihydric, trihydric, or other lower polyalcohols (4-6 hydroxy containing), such as 2-ethyl hexyl stearate, n-butyl oleate, isopropyl myristate, propylene glycol dioleate, di-octyl succinate, di-butyl adipate, di-octyl phthalate and the like; esters of mono, di and polycarboxylic acids and the like. Organic solvents include, but are not limited to toluene, xylene, petroleum naphtha, crop oil, acetone, methyl ethyl ketone, cyclohexanone, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol monomethyl ether and diethylene glycol monomethyl ether, methyl alcohol, ethyl alcohol, isopropyl alcohol, amyl alcohol, ethylene glycol,

propylene glycol, glycerine, N-methyl-2-pyrrolidinone, N,N-dimethyl alkylamides, dimethyl sulfoxide.

- Solid carriers that may be employed in the compositions of the present invention may include but are not limited to attapulgite, pyrophyllite clay, silica, kaolin clay, kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite clay, Fuller's earth, talc, cottonseed hulls, wheat flour, soybean flour, pumice, wood flour, walnut shell flour, lignin, cellulose etc.
- Suitable stabilising agents such as buffers such ammonium phosphate dibasic, ammonium sulfate, ammonium, potassium dibasic phosphate, and the like, other stabilizers such as casein, tragacanth, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA) and the like.
- Thus, in another aspect, the present invention provides a method of controlling weeds at a locus, said method comprising applying a composition comprising at least two synthetic auxins, at least one sulfonylurea herbicide and at least one agrochemically acceptable excipient.
- Surprisingly, it has been found by the present inventors that at least two synthetic auxins and at least an ALS inhibitor herbicide, preferably a sulfonylurea herbicide, when applied individually, was ineffective in the control of weeds, but demonstrated excellent synergistic control on weeds when applied together. The combination controlled the weed both pre and post emergently. The combination of at least two synthetic auxins and at least a sulfonylurea herbicide synergistically controlled broadleaf weeds, sedges, and grasses at a particular locus. The current invention therefore provides advantageous methods of controlling weeds both pre and post emergently. The present method also provides a broader spectrum of controlling weeds that helps in resistance management, thus preventing the weed from becoming resistant to either of the herbicides whilst providing a broader spectrum of control at lower use rates.

## 32

The invention shall now be described with reference to the following specific examples. It should be noted that the example(s) appended below illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the present invention.

5

**EXAMPLES:****FORMULATIONS STUDIES:**

| S. No. | Ingredients                               | Amount (gms/lit, %) | Generic Name               | Function/Role of ingredients |
|--------|-------------------------------------------|---------------------|----------------------------|------------------------------|
| 1      | Picloram ácid tech                        | 96,00               | Picloram ácid tech         | Active Ingredient            |
| 2      | 2,4 D ácid tech                           | 318,00              | 2,4 D ácid tech            | Active Ingredient            |
| 3      | Metsulfuron Methyl tech                   | 45,00               | Metsulfuron Methyl tech    | Active Ingredient            |
| 4      | Ammonium phosphate dibasic                | 451,00              | Ammonium phosphate dibasic | Neutralizing agent           |
| 5      | Sodium dodecylbenzene sulfonate           | 30,0                | Agnique 46 NP              | Wetting agent                |
| 6      | Sulphonated aromatic polymer, sodium salt | 30,0                | Morwet D425                | Dispersant agent             |
| 7      | Croscarmellose sodium                     | 30,0                | Solutab                    | binder                       |

10

The above formulation was also found to solve the technical problem of making metsulfuron molecule compatible with 2,4-D acid and Picloram in the same formulation. Hitherto, all commercially available products of 2,4-D and picloram were in soluble liquid i.e. SL formulation, which entails the use of water as the solvent. However, metsulfuron-methyl degrades rapidly by hydrolysis in the protonic media e.g. in an aqueous solution (DT50/25°C=4.7d, pesticide manual), which makes it incompatible in liquid formulations, mostly in SL type formulation in

15

which water is used as solvent. This posed a formulation problem as 2,4D-DMA and Picloram-DMA are conventionally formulated in liquid water-based formulations. Further, in order to render 2,4D- acid and picloram soluble in water, they need to be neutralized by an organic base, producing a soluble salt in water.

- 5 In an embodiment, Dimethylammonium was used to neutralize these two acid and insoluble active ingredients in water.

In an embodiment, the present invention also provides a combination comprising 2,4-D ammonium and picloram-ammonium.

- 10 In an embodiment, the present invention provides a solid formulation comprising 2,4-D, picloram and metsulfuron-methyl.

In an embodiment, the present invention provides a solid formulation comprising 2,4-D, picloram, metsulfuron-methyl and dibasic ammonium phosphate.

In an embodiment, the present invention provides a solid formulation comprising 2,4-D, picloram, metsulfuron-methyl and sodium dodecylbenzene sulfonate.

- 15 In an embodiment, the present invention provides a solid formulation comprising 2,4-D, picloram, metsulfuron-methyl and sodium salt of sulphonated aromatic polymer.

In an embodiment, the present invention provides a solid formulation comprising 2,4-D, picloram, metsulfuron-methyl and croscarmellose sodium.

- 20 In an embodiment, the present invention provides a wettable granule (WG) formulation comprising 2,4-D, picloram and metsulfuron-methyl.

In an embodiment, the present invention provides a wettable granule (WG) formulation comprising 2,4-D, picloram and metsulfuron-methyl, wherein the formulation has D<sub>90</sub> less than 10 microns.

- 25 Thus, presenting these active ingredients in a solid formulation avoids the contact of metsulfuron-methyl with the aqueous media and thus avoids its degradation. In order to make the WG formulation possible, 2,4-D acid and picloram were neutralized in an unexpected manner according to the present invention.

Thus, according to the present invention, 2,4-D-acid and picloram were *in situ* neutralized in the presence of an alkali salt.

In an embodiment, the preferred alkali salt was dibasic ammonium phosphate.

In an embodiment, the present invention also provides a combination comprising  
5 2,4-D ammonium and picloram-ammonium.

In an embodiment, the present invention also provides a combination comprising 2,4-D ammonium, picloram-ammonium and at least one ALS inhibitor herbicide.

Thus, the alkali salt was mixed into the formulation together with Metsulfuron, 2,4-D acid, and Picloram acid, dispersing/wetting agents and other inerts. All the  
10 ingredients together were milled into a jet mill up to the particle size being reduced to  $d_{90} < 10$  microns. To make the dough from this milled powder, a rigorous control of adding minimum water with vigorous mixing process is required. Extrusion of the dough was done with a conventional screw extruder, and granules were dried in the sequence of process until reach moisture contain less than 2%. Fluid bed dryer  
15 at 54°C is used to remove water from granules.

These wettable granule formulation (WG) were applied into the crops after being diluted into the spray solution.

It was found that the alkali salt ammonium phosphate dibasic reacted with 2,4-D acid (solubility= 311 mg/l) and Picloram acid (solubility= 560 mg/l), producing 2,4-  
20 D ammonium salt and Picloram ammonium salt, thereby increasing solubility of both active ingredients into this spray solution.

It was concluded that one of the advantages of the present invention was to render 2,4-D and picloram acids to corresponding salts to make those active ingredients soluble, which resulted into good and uniform application in crops. In the absence  
25 of the alkali salts of the invention, the insoluble 2,4-D and picloram acid active ingredients did not have good biological performance and blocked nozzles during spraying.

The formulations of the present invention were then subjected to the efficacy studies.

### **SYNERGY STUDIES**

Studies were conducted to compare the weed controlling activity of the combination of at least two synthetic auxins and at least one sulfonylurea herbicide and compared the observed efficacy with the “expected” efficacy. Any difference between the observed and “expected” efficacy could be attributed to synergy between the compounds. The synthetic auxins were picloram and 2,4-D, whereas, the sulfonylurea was metsulfuron methyl. The expected efficacy of the combination was calculated using the well-established Colby method.

In the Colby method, the expected (or predicted) response of a combination of herbicides is calculated by taking the product of the observed response for each individual component of the combination when applied alone divided by 100 and subtracting this value from the sum of the observed response for each component when applied alone. An unexpected enhancement in efficacy of the combination is then determined by comparing the observed response of the combination to the expected (or predicted) response as calculated from the observed response of each individual component alone. If the observed response of the combination is greater than the expected (or predicted) response, or stated conversely, if the difference between the observed and expected response is greater than zero, then the combination is said to be synergistic or unexpectedly effective. (Colby, S. R., Weeds, 1967(15), p. 20-22) The Colby method requires only a single dose of each herbicide applied alone and the mixture of both doses. The formula used to calculate the expected efficacy (EE) which was compared with the observed efficacy (OE) to determine the efficacy of the present invention is explained hereinbelow:

$$EE = (B \text{ efficacy} + A \text{ efficacy} - (B \text{ efficacy} \times A \text{ efficacy}) / 100)$$

The weed control activity of the individual herbicides of the invention and their combinations were evaluated on weeds such as *Ipomea grandifolia* and *Bidens pilosa* in cotton was evaluated. The trial was carried out in Randomized Complete Block (RCB) method, all field trials were conducted using this method. Each trial  
 5 were replicated four times and conducted under GEP guidelines. Application volumes were varied for each mixture. Such field trials were carried out at various locations so as to generate independent data, the locations were chosen randomly across Brazil. Picloram, 2,4-D acid and 2,4-D sodium and Metsulfuron methyl were sprayed according to their recommended dosage.

10

The following formula was used to calculate the expected activity of mixtures containing three active ingredients A, B and C:

$$\text{Expected (E)} = A + B + C - \frac{(AB+AC+BC)}{100} + \frac{ABC}{10,000}$$

Where

15 A = observed efficacy of active ingredient A at the same concentration as used in the mixture.

B = observed efficacy of active ingredient B at the same concentration as used in the mixture.

20 C = observed efficacy of active ingredient C at the same concentration as used in the mixture.

The herbicide tank mix combinations, application rates, plant species tested, and results are given in the following examples:

### **Example:**

25 In the Colby method, the expected (or predicted) response of a combination of herbicides is calculated by taking the product of the observed response for each individual component of the combination when applied alone divided by 100 and subtracting this value from the sum of the observed response for each component

when applied alone. An unexpected enhancement in efficacy of the combination is then determined by comparing the observed response of the combination to the expected (or predicted) response as calculated from the observed response of each individual component alone. If the observed response of the combination  
5 is greater than the expected (or predicted) response, or stated conversely, if the difference between the observed and expected response is greater than zero, then the combination is said to be synergistic or unexpectedly effective.

Thus, when the combination of the present invention was analyzed using this method, it demonstrated an observed – expected value of greater than zero which  
10 is indicative of an unexpected efficacy. The basis of demonstration of unexpected efficacy by comparison with the Colby formula is that herbicide (A) tested alone would kill a proportion of the target weeds and leave the remaining portion (a%) as survivors. Similarly, herbicide B tested alone will leave (b%) as survivors, and herbicide B tested alone will leave (c%) survivors. When combined, A+B+C will,  
15 act independently on the target weed (if unexpected activity is absent); component A leaving a% survivors, which survivors will be controlled by component B and the final survivors being controlled by component C; which has an overall effect of  $a\% \cdot b\% \cdot c\% \cdot 100$ . Subsequently, if the percent control is greater than that predicted by the Colby formula or stated conversely, if the difference between the observed  
20 control and the expected control is greater than zero; then unexpected enhancement in activity is acknowledged. The degree to which the difference is greater than zero is not itself critical as long as it is greater than zero; however greater the difference, more significant is the enhancement or the unexpectedness in weed control.

25 A trial was carried out to check the efficacy of the triple mixture herbicide of the present invention for pasture. Trials were also carried out to check the efficacy of the formulation examples above. The formulation examples were carried out to evaluate the efficacy of two WG formulations of the 2,4-D, picloran and metsulfuron mixture (PED015/16 and PED016/16) for weeds control in pasture compared with  
30 the commercial products in tank mixture. These trials were carried out under greenhouse conditions for efficacy studies. The efficacy for *Ipomea grandifolia* and

## 38

*Bidens pilosa* control in cotton was tested. The two WG formulations which were tested were PED015/16 and PED016/16. PED015/16 was the formulation comprising Picloram (96) + 2,4-D **acid** (318) + Metsulfuron (45); whereas PED016/16 comprised Picloram (96) + 2,4-D **sodium** (318) + Metsulfuron (45).

5

Thus, in an embodiment, the present invention provides a combination comprising picloram at 96 g per hectare, 2,4-D acid at 318 g per hectare and metsulfuron-methyl at 45 g per hectare.

- 10 In an embodiment, the present invention provides a combination comprising picloram at 96 g per hectare, 2,4-D sodium at 318 g per hectare and metsulfuron-methyl at 45 g per hectare.

| Product                     | Dose (g or mL per hectare) [g a.e. per hectare] | 7 DAA     |               | 14 DAA    |               | 21 DAA    |               | Conclusion                                |
|-----------------------------|-------------------------------------------------|-----------|---------------|-----------|---------------|-----------|---------------|-------------------------------------------|
|                             |                                                 | % Control | Colby control | % control | Colby control | % control | Colby control |                                           |
| Donado (Picloram)           | 200.0 [48]                                      | 23.3      | -             | 22.3      | -             | 30.0      | -             | -                                         |
| DMA (2,4-D)                 | 237.3 [159]                                     | 21.7      | -             | 22.7      | -             | 27.7      | -             | -                                         |
| Zartan (Metsulfuron-methyl) | 37.5 [22.5]                                     | 8.7       | -             | 20.7      | -             | 22.0      | -             | -                                         |
| PED015/16                   | 0.5 [48 + 159 + 22.5]                           | 55.0      | 45.2          | 94.7      | 52.4          | 98.7      | 60.5          | Synergistic ( $\Delta$ is greater than 0) |
| PED016/16                   | 0.5 [48 + 159 + 22.5]                           | 58.7      | 45.2          | 95.7      | 99.3          | 99.3      | 60.5          | Synergistic ( $\Delta$ is greater than 0) |
| Donado + DMA + Zartan       | 0.5 [48 + 159 + 22.5]                           | 51.0      | 45.2          | 90.7      | 52.4          | 95.7      | 60.5          | Synergistic ( $\Delta$ is greater than 0) |

- 15 Thus, in an embodiment, the present invention provides a combination comprising picloram at 48 g per hectare, 2,4-D acid at 159 g per hectare and metsulfuron-methyl at 22.5 g per hectare.

In an embodiment, the present invention provides a combination comprising picloram at 48 g per hectare, 2,4-D sodium at 159 g per hectare and metsulfuron-methyl at 22.5 g per hectare.

- 5 It was thus found that, under the tested conditions, both formulations PED015/16 and PED016/16 were effective for control of the studied plants (*Cotton*, *Ipomea grandifolia* and *Bidens pilosa*) at all doses.

10 In an embodiment, the present invention provides a method of controlling *Ipomea grandifolia* and *Bidens pilosa*, said method comprising applying a combination comprising picloram at 48 g per hectare, 2,4-D acid at 159 g per hectare and metsulfuron-methyl at 22.5 g per hectare to the locus.

15 In an embodiment, the present invention provides a method of controlling *Ipomea grandifolia* and *Bidens pilosa* in cotton, said method comprising applying a combination comprising picloram at 48 g per hectare, 2,4-D acid at 159 g per hectare and metsulfuron-methyl at 22.5 g per hectare to the locus.

20 In an embodiment, the present invention provides a method for controlling *Ipomea grandifolia* and *Bidens pilosa*, said method comprising applying a combination comprising picloram at 48 g per hectare, 2,4-D sodium at 159 g per hectare and metsulfuron-methyl at 22.5 g per hectare to the locus.

25 In an embodiment, the present invention provides a method for controlling *Ipomea grandifolia* and *Bidens pilosa* in cotton, said method comprising applying a combination comprising picloram at 48 g per hectare, 2,4-D sodium at 159 g per hectare and metsulfuron-methyl at 22.5 g per hectare to the locus.

30 The tank mix at the lowest dose did not control *Ipomoea grandifolia*. In terms of efficacy, both the tested formulations PED015/16 and PED016/16 showed higher efficiency than the tank mix. It was thus concluded that the combinations of the present invention demonstrated proven synergy for the two formulated

## 40

combinations and tank mix at the lowest dose for cotton control according to the Colby formula in the evaluations at 7, 14 and 21 DAA.

It was also noted that the formulation containing 2,4-D acid form displayed changes  
5 in the volatility of the herbicide and thus the salt form may be preferred for some agronomists.

While the foregoing written description of the invention enables one of ordinary skill to make and use what is considered presently to be the best mode thereof, those  
10 of ordinary skill will understand and appreciate the existence of variations, combinations, and equivalents of the specific embodiment, method, and examples herein. The invention should therefore not be limited by the above described embodiment, method, and examples, but by all embodiments and methods within the scope and spirit of the invention.

15

20

**CLAIMS**

1. A herbicidal combination comprising at least two synthetic auxin herbicides and at least one ALS inhibitor herbicide.
- 5 2. The combinations as claimed in claim 1, wherein at least two auxin herbicides are selected from the group consisting of (2,4-D); 2,4-DB; dicamba; chloramben; 2,4,5-T; clomeprop; dichlorprop; dichlorprop-P; MCPA; MCPB; mecoprop; aminopyralid; clopyralid; fluroxypyr; halauxifen-methyl; picloram; triclopyr; aminocyclopyrachlor; quinclorac; quinmerac and  
10 their salts; and esters thereof.
3. The combination as claimed in claim 1 or claim 2, wherein the synthetic auxins are selected from the group consisting of 2,4-D and dicamba; 2,4-D and MCPA; 2,4-D and fluroxypyr; 2,4-D and halauxifen-methyl; 2,4-D and  
15 picloram; 2,4-D and triclopyr; 2,4-D and quinclorac; 2,4-D and quinmerac; dicamba and MCPA; dicamba and fluroxypyr; dicamba and halauxifen-methyl; dicamba and picloram; dicamba and triclopyr; dicamba and quinclorac; dicamba and quinmerac; MCPA and fluroxypyr; MCPA and  
20 halauxifen-methyl; MCPA and picloram; MCPA and triclopyr; MCPA and quinclorac; MCPA and quinmerac; fluroxypyr and halauxifen-methyl; fluroxypyr and picloram; fluroxypyr and triclopyr; fluroxypyr and quinclorac; fluroxypyr and quinmerac; halauxifen-methyl and picloram; halauxifen-methyl and triclopyr; halauxifen-methyl and quinclorac; halauxifen-methyl  
25 and quinmerac; picloram and triclopyr; picloram and quinmerac; picloram and quinclorac; triclopyr and quinclorac; triclopyr and quinmerac; and quinclorac and quinmerac; and their salts or esters thereof.
4. The combinations as claimed in claims 1 – 3, wherein the ALS inhibitor is  
30 selected from sulfonylurea herbicides, or imidazolinone herbicides, triazolopyrimidine herbicides, and pyrimidinyl thiobenzoate herbicides, wherein:

## 42

the sulfonylurea herbicide is selected from the group consisting of  
amidosulfuron, azimsulfuron, bensulfuron, chlorimuron, cyclosulfamuron,  
ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron,  
5 halosulfuron, imazosulfuron, mesosulfuron, metazosulfuron,  
methiopyrisulfuron, monosulfuron, nicosulfuron, orthosulfamuron,  
oxasulfuron, primisulfuron, propyrisulfuron, pyrazosulfuron, rimsulfuron  
,sulfometuron, sulfosulfuron, trifloxysulfuron, zuomihuanglong,  
chlorsulfuron, cinosulfuron, ethametsulfuron, iodosulfuron, iofensulfuron,  
10 metsulfuron, prosulfuron, thifensulfuron, triasulfuron, tribenuron,  
triflusulfuron, and tritosulfuron;

the imidazolinone herbicide is selected from the group consisting of  
imazamethabenz, imazamox, imazapic, imazapyr, imazaquin and  
15 imazethapyr;

the triazolopyrimidine herbicide is selected from the group consisting of  
chloransulam, diclosulam, florasulam, flumetsulam, metosulam,  
penoxsulam and pyroxsulam; and  
20

the pyrimidinyl benzoic acid herbicide is selected from bispyribac,  
pyriminobac and pyriithiobac.

5. A herbicidal combination comprising 2,4-D acid or a salt thereof, picloram  
25 acid or a salt thereof and metsulfuron or an ester thereof.

6. A composition comprising the combination as claimed in claims 1 – 5, and  
at least one agrochemically acceptable excipient or adjuvant.

30 7. A method of controlling weeds at a locus, said method comprising applying  
the combination as claimed in claims 1 – 5 to the locus of said weed.

## 43

8. A kit having its components comprising one or more of the active ingredients of the combinations claimed in claims 1 – 5.
9. A combination comprising 2,4-D ammonium and picloram-ammonium.
- 5 10. The combination as claimed in claim 9, comprising at least another ALS inhibitor herbicide.
- 10 11. A solid formulation comprising 2,4-D, picloram, metsulfuron-methyl and dibasic ammonium phosphate.

## INTERNATIONAL SEARCH REPORT

 International application No.  
**PCT/IB2018/055716**

## A. CLASSIFICATION OF SUBJECT MATTER

**A01N 39/04 (2006.01) A01N 47/36 (2006.01) A01N 43/40 (2006.01) A01P 13/00 (2006.01)**

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)

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)

Classification symbols - A01N39/04, A01N47/36, A01N43/40

Databases - CAPLUS, REGISTRY, BIOSIS, CABA, EMBASE, INFULL, KRFULL, JPFULL, CNFULL, GOOGLE, GOOGLE SCHOLAR, GOOGLE PATENT, logical database - PATENW

Keywords - Synthetic Auxin herbicides, ALS inhibitor herbicides, picloram, metsulfulam, 2,4-D, herbicides, synergy, combinations, ternary, TORDON 75-D and like terms

Applicant/Inventor Search UPL LTD, BRITO, DE ALMEIDA, SILVA, DA CUNHA, HOHMANN, GONCALVES, DECARO JUNIOR, SHROFF.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
|           | Documents are listed in the continuation of Box C                                  |                       |



Further documents are listed in the continuation of Box C



See patent family annex

|          |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |
|----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| *<br>"A" | Special categories of cited documents:<br>document defining the general state of the art which is not considered to be of particular relevance                      | "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                                              |
| "E"      | earlier application or patent but published on or after the international filing date                                                                               | "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                                                                     |
| "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) | "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 |
| "O"      | document referring to an oral disclosure, use, exhibition or other means                                                                                            | "&" | document member of the same patent family                                                                                                                                                                                                    |
| "P"      | document published prior to the international filing date but later than the priority date claimed                                                                  |     |                                                                                                                                                                                                                                              |

|                                                                                                                                                                |                                                                                                                                              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| Date of the actual completion of the international search<br>26 September 2018                                                                                 | Date of mailing of the international search report<br>26 September 2018                                                                      |
| <b>Name and mailing address of the ISA/AU</b><br><br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>Email address: pct@ipaustalia.gov.au | <b>Authorised officer</b><br><br>Karl Heys<br>AUSTRALIAN PATENT OFFICE<br>(ISO 9001 Quality Certified Service)<br>Telephone No. +61262832725 |

| INTERNATIONAL SEARCH REPORT                           |                                                                                                                                                                                                                                                                                                                                                           | International application No. |
|-------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|
| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                           | PCT/IB2018/055716             |
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                        | Relevant to claim No.         |
| X                                                     | Herbguide combination 'Metsulfuron 200 plus Picloram 240' [retrieved from internet on 21 September 2018]<br><URL:http://www.herbguide.com.au/Descriptions/hg_Metsulfuron_200_plus_Picloram_240.htm> published on 26 August 2011 as per Wayback Machine.<br>top of page as cited prior to 3                                                                | 1-11                          |
| X                                                     | CIMARRON MAX herbicide, BAYER, [retrieved from internet on 17 September 2018]<br><URL:https://www.backedbybayer.com/~media/BackedByBayer/Product%20Labels%20-%20pdf/Cimarron%20Max.ashx> published on 05 December 2015 as per Wayback Machine.<br>page 1 of document.                                                                                     | 1-4 & 6-8                     |
| X                                                     | US 2014/0256552 A1 (DOW AGROSCIENCES LLC) 11 September 2014<br>Whole of document but especially Abstract, claims, paragraphs [0030] & [0032]-[0038]                                                                                                                                                                                                       | 1-4 & 6-8                     |
| X                                                     | US 2011/0092366 A1 (GRIVEAU et al.) 21 April 2011<br>Abstract, claims, table 2                                                                                                                                                                                                                                                                            | 1-4, 6-8                      |
| X                                                     | CN 104542663 A (JIANGXI ZHONGXUN AGROCHEMICAL CO LTD) 29 April 2015<br>Abstract, claims, examples                                                                                                                                                                                                                                                         | 1-4, 6-8                      |
| X                                                     | CN 106472529 A (SICHUAN LIER CROP SCIENCES CO LTD) 08 March 2017<br>Abstract, exemplified                                                                                                                                                                                                                                                                 | 1-4 & 6-7.                    |
| X                                                     | HUMPHRYS, M. et al. 'Control options for Rubber Bush' DEPARTMENT OF LAND RESOURCE MANAGEMENT, Northern Territory Government [retrieved from internet on 17 September 2018]<br><https://denr.nt.gov.au/__data/assets/pdf_file/0006/257991/control-options-rubber-bush.pdf> published on 09 March 2017 as per Wayback Machine.<br>results -point 4, table 1 | 1-4 & 6-7.                    |
| X                                                     | Tordon 75-D herbicide Label, DOW AGROSCIENCES LLC [retrieved from internet on 21 September 2018] <URL:http://www.dowagro.com/en-au/australia/product_finder/herbicides/tordon-75d> published on 24 January 2016 as per Wayback Machine.<br>page 1                                                                                                         | 9-10                          |
| Form PCT/ISA/210 (fifth sheet) (January 2015)         |                                                                                                                                                                                                                                                                                                                                                           |                               |

**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:  
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
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 Supplemental Box for Details**

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 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.:

**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.

**Supplemental Box****Continuation of: Box III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-8 & 10-11 is directed to an at least 3 part herbicidal combination comprising 2 synthetic auxin herbicides and an ALS inhibitor herbicide. The feature of a ternary combination containing 2 auxin herbicides and at least one ALS inhibitor is specific to this group of claims.
- Claims 9 is directed to a binary herbicidal combination. The feature of this combination comprising picloram ammonium salt and 2,4-D ammonium salt is specific to this group of claims

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is the presence of 2 synthetic auxin herbicides in the combination. However this feature does not make a contribution over the prior art because it is disclosed in:

D2- CIMARRON MAX herbicide (BAYER) published on 05 December 2015 as per Wayback Machine.

Or alternatively any of D1 or D3-D7

Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

| INTERNATIONAL SEARCH REPORT                                                                                                                                                                                                                                           |                   | International application No. |                  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|-------------------------------|------------------|
| Information on patent family members                                                                                                                                                                                                                                  |                   | PCT/IB2018/055716             |                  |
| This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information. |                   |                               |                  |
| Patent Document/s Cited in Search Report                                                                                                                                                                                                                              |                   | Patent Family Member/s        |                  |
| Publication Number                                                                                                                                                                                                                                                    | Publication Date  | Publication Number            | Publication Date |
| US 2014/0256552 A1                                                                                                                                                                                                                                                    | 11 September 2014 | US 2014256552 A1              | 11 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                   | US 8999891 B2                 | 07 Apr 2015      |
|                                                                                                                                                                                                                                                                       |                   | AU 2014225854 A1              | 27 Aug 2015      |
|                                                                                                                                                                                                                                                                       |                   | AU 2014225854 B2              | 17 Nov 2016      |
|                                                                                                                                                                                                                                                                       |                   | CA 2901341 A1                 | 12 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                   | EP 2964031 A1                 | 13 Jan 2016      |
|                                                                                                                                                                                                                                                                       |                   | JP 2016509071 A               | 24 Mar 2016      |
|                                                                                                                                                                                                                                                                       |                   | JP 6360504 B2                 | 18 Jul 2018      |
|                                                                                                                                                                                                                                                                       |                   | WO 2014138177 A1              | 12 Sep 2014      |
| US 2011/0092366 A1                                                                                                                                                                                                                                                    | 21 April 2011     | US 2011092366 A1              | 21 Apr 2011      |
|                                                                                                                                                                                                                                                                       |                   | US 8809233 B2                 | 19 Aug 2014      |
|                                                                                                                                                                                                                                                                       |                   | AU 2009259383 A1              | 23 Dec 2009      |
|                                                                                                                                                                                                                                                                       |                   | AU 2009259383 B2              | 18 Sep 2014      |
|                                                                                                                                                                                                                                                                       |                   | BR PI0914206 A2               | 11 Aug 2015      |
|                                                                                                                                                                                                                                                                       |                   | CA 2725375 A1                 | 23 Dec 2009      |
|                                                                                                                                                                                                                                                                       |                   | EA 201100008 A1               | 30 Aug 2011      |
|                                                                                                                                                                                                                                                                       |                   | EA 021466 B1                  | 30 Jun 2015      |
|                                                                                                                                                                                                                                                                       |                   | EP 2296466 A2                 | 23 Mar 2011      |
|                                                                                                                                                                                                                                                                       |                   | EP 2296466 B1                 | 19 Mar 2014      |
|                                                                                                                                                                                                                                                                       |                   | EP 2740358 A1                 | 11 Jun 2014      |
|                                                                                                                                                                                                                                                                       |                   | EP 2740358 B1                 | 21 Feb 2018      |
|                                                                                                                                                                                                                                                                       |                   | EP 2740359 A1                 | 11 Jun 2014      |
|                                                                                                                                                                                                                                                                       |                   | EP 2740359 B1                 | 21 Feb 2018      |
|                                                                                                                                                                                                                                                                       |                   | EP 2740360 A1                 | 11 Jun 2014      |
|                                                                                                                                                                                                                                                                       |                   | EP 2740360 B1                 | 06 Dec 2017      |
|                                                                                                                                                                                                                                                                       |                   | EP 2742802 A1                 | 18 Jun 2014      |
|                                                                                                                                                                                                                                                                       |                   | RS 53312 B                    | 31 Oct 2014      |
|                                                                                                                                                                                                                                                                       |                   | US 2014309110 A1              | 16 Oct 2014      |
|                                                                                                                                                                                                                                                                       |                   | US 2014309111 A1              | 16 Oct 2014      |
|                                                                                                                                                                                                                                                                       |                   | WO 2009153246 A2              | 23 Dec 2009      |
| CN 104542663 A                                                                                                                                                                                                                                                        | 29 April 2015     | CN 104542663 A                | 29 Apr 2015      |
| Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.                                                                                                                                             |                   |                               |                  |

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(January 2015)

|                                                                                                                                                                                                                                                                       |                         |                                                           |                         |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|-----------------------------------------------------------|-------------------------|
| <b>INTERNATIONAL SEARCH REPORT</b><br>Information on patent family members                                                                                                                                                                                            |                         | International application No.<br><b>PCT/IB2018/055716</b> |                         |
| This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information. |                         |                                                           |                         |
| <b>Patent Document/s Cited in Search Report</b>                                                                                                                                                                                                                       |                         | <b>Patent Family Member/s</b>                             |                         |
| <b>Publication Number</b>                                                                                                                                                                                                                                             | <b>Publication Date</b> | <b>Publication Number</b>                                 | <b>Publication Date</b> |
| CN 106472529 A                                                                                                                                                                                                                                                        | 08 March 2017           | CN 106472529 A                                            | 08 Mar 2017             |
| <b>End of Annex</b>                                                                                                                                                                                                                                                   |                         |                                                           |                         |
|                                                                                                                                                                                                                                                                       |                         |                                                           |                         |
| Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.                                                                                                                                             |                         |                                                           |                         |