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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 February 2015 (12.02.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/019355 A1

(51) International Patent Classification:
*A01N 43/40* (2006.01) *A01P 13/00* (2006.01)
*A01N 37/40* (2006.01)

(21) International Application Number:
PCT/IL2014/050713

(22) International Filing Date:
6 August 2014 (06.08.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/862,682 6 August 2013 (06.08.2013) US

(71) Applicant: **ADAMA AGAN LTD.** [IL/IL]; P.O. Box 262, Northern Industrial Zone, 77102 Ashdod (IL).

(72) Inventors: **KERGOAT, Pierre-Yves**; 11 rue Bichat, F-75010 Paris (FR). **HORSFIELD, Andrew**; 43 Twenty-Third Avenue, Brighton, Queensland (AU).

(74) Agents: **EHRLICH, Gal** et al.; G.E. EHRLICH (1995) LTD., 11 Menachem Begin Road, 5268104 Ramat Gan (IL).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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**:

— *of inventorship (Rule 4.17(iv))*

**Published**:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2015/019355 A1

(54) Title: SYNERGISTIC HERBICIDAL MIXTURE

(57) Abstract: The present subject matter relates to a ternary synergistic herbicidal mixture for controlling undesired vegetation. The synergistic mixture comprises an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, or a combination thereof.

# SYNERGISTIC HERBICIDAL MIXTURE

## CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S Provisional Application No. 61/862,682, filed August 6, 2013, which is hereby incorporated by reference herein in its entirety.

## PRESENT SUBJECT MATTER

The present subject matter relates to a ternary herbicidal mixture for controlling undesired vegetation.

## BACKGROUND OF THE PRESENT SUBJECT MATTER

The control of undesired vegetation is extremely important in order to achieve high crop efficiency. In many cases, while herbicides have an effect against a spectrum of weeds, they do not however fight a certain type of other weeds, which is also present in the crop cultures to be protected. Therefore, there is a strong need for mixing two or more herbicides.

Mixtures of selected herbicides have several advantages over the use of a single herbicide including (a) an increase in the spectrum of weeds controlled or an extension of weed control over a longer period of time, (b) an improvement in crop safety by using minimum doses of selected herbicides applied in combination rather than a single high dose of one herbicide, and (c) a delay in the appearance of resistant weed species to selected herbicides (*Int. J. Agri. Biol., Vol. 6, No. 1, 2004*, pages 209-212).

However, the activity and selectivity behavior of any specific mixture is difficult to predict since the behavior of each single herbicide in the mixture is often affected by the presence of the other(s) and the activity of the mixture may also vary considerably depending on chemical character, plant species, growth stage, and environmental conditions. Mostly, this practice results in reduced activity of the herbicides in the mixture.

Diflufenican was first described by M. C. C. Ramp *et al.* (*Proc. Br. Crop Prot. Conf. - Weeds,* 1985, **1,** 23).

Bromoxynil was first described by R. L. Wain (*Nature (London)*, 1963, **200,** 28).

Fluroxypyr was first described by O. Visbecq *et al.* (Proc. COLUMA Conf., 1983, p. 257).

## SUMMARY OF THE PRESENT SUBJECT MATTER

According to one aspect, the present subject matter provides a synergistic herbicidal mixture comprising an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof.

According to another aspect, the present subject matter provides a composition comprising a mixture of an Auxin type herbicide, bromoxynil, and diflufenican or an ester or salt of any of the foregoing, and/or a combination thereof; and at least one agriculturally acceptable carrier.

According to yet another aspect, the present subject matter provides a method of controlling undesired vegetation comprising applying to a locus of the undesired vegetation a herbicidal effective amount of a mixture comprising an Auxin type herbicide, bromoxynil and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof.

## DETAILED DESCRIPTION OF THE PRESENT SUBJECT MATTER

### Definitions

Prior to setting forth the present subject matter in detail, it may be helpful to provide definitions of certain terms to be used herein. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this subject matter pertains.

As used herein, the phrase "agriculturally acceptable carrier" means carriers which are known and accepted in the art for the formation of formulations for agricultural or horticultural use.

As used herein, the term "crop" includes reference to a whole plant, plant organ (e.g., leaves, stems, twigs, roots, trunks, limbs, shoots, fruits etc.), plant cells, or plant seeds.

As used herein, the term "locus" includes not only areas where weeds may

already be growing, but also areas where weeds have yet to emerge, and also to areas under cultivation.

As used herein, the term "mixture" or "combination" refers, but is not limited to, a combination in any physical form, e.g., blend, solution, alloy, or the like.

The term "a" or "an" as used herein includes the singular and the plural, *unless specifically stated* otherwise. Therefore, the terms "a," "an" or "at least one" can be used interchangeably in this application.

Throughout the application, descriptions of various embodiments use the term "comprising"; however, it will be understood by one of skill in the art, that in some specific instances, an embodiment can alternatively be described using the language "consisting essentially of" or "consisting of."

For purposes of better understanding the present teachings and in no way limiting the scope of the teachings, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained. At the very least, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. In this regard, use of the term "about" herein specifically includes ±10% from the indicated values in the range. In addition, the endpoints of all ranges directed to the same component or property herein are inclusive of the endpoints, are independently combinable, and include all intermediate points and ranges.

Synergistic Herbicidal Mixture

The present subject matter relates to a synergistic herbicidal mixture comprising an Auxin type herbicide, bromoxynil and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof.

Suitable non limiting examples of an Auxin type herbicide useful in this regard include fluroxypyr, MCPA, 2,4 D, aminopyralid, clopyralid, picloram, triclopyr esters, and salts and/or combinations thereof.

In one embodiment, the Auxin type herbicide is fluroxypyr.

In a specific embodiment, the Auxin type herbicide is fluroxypyr meptyl.

In a further embodiment, the Auxin type herbicide is MCPA.

In a further specific embodiment, the Auxin type herbicide is MCPA 2-ethyl hexyl ester.

In one embodiment, the present subject matter relates to a synergistic herbicidal mixture of fluroxypyr, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof. In a specific embodiment, the present subject matter relates to a synergistic herbicidal mixture of bromoxynil octanoate, diflufenican, and fluroxypyr meptyl.

In one embodiment, the present subject matter relates to a synergistic herbicidal mixture of MCPA, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof. In a specific embodiment, the present subject matter relates to a synergistic herbicidal mixture of bromoxynil octanoate, diflufenican, and MCPA 2-ethyl hexyl ester.

In one embodiment, the weight ratio of diflufenican to the Auxin type herbicide in the mixture is from about 1:30 to 30:1. In another embodiment, the weight ratio of diflufenican to the Auxin type herbicide is from about 1:10 to 10:1. In yet another embodiment, the weight ratio of diflufenican to the Auxin type herbicide is from about 1:5 to 5:1. In yet another embodiment, the weight ratio of diflufenican to the Auxin type herbicide is from about 1:2 to 2:1.

In another embodiment, the weight ratio of diflufenican to fluroxypyr meptyl in the mixture is from about 1:30 to 30:1. In a further embodiment, the weight ratio of diflufenican to fluroxypyr meptyl is from about 1:10 to 10:1. In yet another embodiment, the weight ratio of diflufenican to fluroxypyr meptyl is from about 1:5 to 5:1. In still another embodiment, the weight ratio of diflufenican to fluroxypyr meptyl is from about 1:2 to 2:1. In a specific embodiment, the weight ratio of diflufenican to fluroxypyr meptyl is about 1: 2.

In another embodiment, the weight ratio of diflufenican to MCPA in the mixture is from about 1:30 to 30:1. In a further embodiment, the weight ratio of diflufenican to MCPA is from about 1:10 to 10:1. In yet another embodiment, the weight ratio of diflufenican to MCPA is from about 1:8 to 8:1. In still another embodiment, the weight

ratio of diflufenican to MCPA is from about 1:2 to 2:1. In a specific embodiment, the weight ratio of diflufenican to MCPA is about 1:10. In a further specific embodiment, the weight ratio of diflufenican to MCPA is about 1:8.

In a further embodiment, the weight ratio of bromoxynil octanoate to the Auxin type herbicide in the mixture is from about 1:10 to 10:1. In another embodiment, the weight ratio of bromoxynil octanoate to the Auxin type herbicide is from about from 1:5 to 5:1. In yet another embodiment, the weight ratio of bromoxynil octanoate to the Auxin type herbicide is from about 1:2 to 2:1. In still another embodiment, the weight ratio of bromoxynil octanoate to the Auxin type herbicide is from about 1:1.5 to 1.5:1.

In another embodiment, the weight ratio of bromoxynil octanoate to fluroxypyr meptyl in the mixture is from about 1:10 to 10:1. In yet another embodiment, the weight ratio of bromoxynil octanoate to fluroxypyr meptyl is from about 1:5 to 5:1. In still another embodiment, the weight ratio of bromoxynil octanoate to fluroxypyr meptyl is from about 1:2 to 2:1. In a further embodiment, the weight ratio of bromoxynil octanoate to fluroxypyr meptyl is from about 1:1.5 to 1.5:1. In a specific embodiment, the weight ratio of bromoxynil octanoate to fluroxypyr meptyl is about 1.5:1. In yet another specific embodiment, the weight ratio of bromoxynil octanoate to fluroxypyr meptyl is about 3:1.

In another embodiment, the weight ratio of bromoxynil octanoate to MCPA in the mixture is from about 1:10 to 10:1. In yet another embodiment, the weight ratio of bromoxynil octanoate to MCPA is from about 1:5 to 5:1. In still another embodiment, the weight ratio of bromoxynil octanoate to MCPA is from about 1:2 to 2:1. In a specific embodiment, the weight ratio of bromoxynil octanoate to MCPA is about 1:1.67. In a further specific embodiment, the weight ratio of bromoxynil octanoate to MCPA is about 1.25:1.

In an embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and the Auxin type herbicide is about 0.5 - 10 : 1 - 10 : 1 – 30, respectively.

In another embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and the Auxin type herbicide is about 0.5 - 5 : 1 - 10 : 1 – 10, respectively.

In yet another embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and fluroxypyr meptyl is about 0.5 - 10 : 1 - 10 : 1 – 30, respectively.

In still another embodiment, the weight ratio between diflufenican, bromoxynil

octanoate, and fluroxypyr meptyl is about 0.5 - 5 : 1 - 10 : 1 – 10, respectively.

In yet another embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and MCPA is about 0.5 - 10 : 1 - 10 : 1 – 30, respectively.

In still another embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and MCPA is about 0.5 - 5 : 1 - 10 : 1 – 10, respectively.

In a specific embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and fluroxypyr meptyl is about 1:3:2. In another specific embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and fluroxypyr meptyl is about 1:3:1. In another specific embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and fluroxypyr meptyl is about 1:2:1.3. In yet another specific embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and fluroxypyr meptyl is about 1.5:3:1.

In a specific embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and MCPA is about 1:6:10. In another specific embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and MCPA is about 1:10:8. In yet another specific embodiment, the weight ratio between diflufenican, bromoxynil octanoate, and MCPA is about 1:8:10.

The present subject matter further relates to a composition comprising an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof; and an agriculturally acceptable carrier.

In a specific embodiment, the present subject matter further relates to a composition comprising fluroxypyr meptyl, bromoxynil octanoate, and diflufenican; and an agriculturally acceptable carrier.

In a specific embodiment, the present subject matter further relates to a composition comprising MCPA, bromoxynil octanoate, and diflufenican; and an agriculturally acceptable carrier.

In yet another embodiment, the composition comprises at least one additional component selected from the group of surfactants, solid diluents and liquid diluents.

The present compositions may include additional crop protection agents, for example pesticides, safeners, or agents for controlling phytopathogenic fungi or bacteria. However, for the avoidance of doubt it is understood that such additional crop protection agents are unnecessary to achieve the synergistic effects of the present

combinations. Accordingly, the present herbicidal compositions and herbicidal mixtures may be limited to containing an Auxin type herbicide, a bromoxynil, and diflufenican as the only crop protection agents and/or herbicides present.

The present compositions can be made at the time of use, or diluted. The present compositions can also be concentrated compositions, or so-called "ready-to-use" compositions, that is to say, compositions ready for use.

The present compositions may be employed or prepared in any conventional form, for example, in the form of a twin pack, or as emulsion concentrates (EC), microemulsion concentrates (MEC), suspension concentrates (SC), soluble concentrates (SL), suspoemulsion (SE), oil dispersions (OD), water dispersible granules (WDG), water soluble granules (SG), or wettable powders (WP). Such compositions can be formulated using agriculturally acceptable carriers, surfactants or other application-promoting adjuvants customarily employed in formulation technology and formulation techniques that are known in the art.

In an embodiment, the amount of the mixture of active ingredients in the composition is about 0.1-99 wt. %, about 0.1-95 wt. %, or about 0.1-90 wt. %, based on the total weight of the composition. In another embodiment, the amount of the mixture of active ingredients in the composition is about 40-80 wt %, based on the total weight of the composition. In another embodiment, the amount of the mixture of active ingredients in the composition is about 0.1-50 wt %, based on the total weight of the composition.

In a specific embodiment, the amount of the mixture of active ingredients in the composition is about 27 wt %, based on the total weight of the composition. In another specific embodiment, the amount of the mixture of active ingredients in the composition is about 64 wt %, based on the total weight of the composition. In yet another specific embodiment, the amount of the mixture of active ingredients in the composition is about 70 wt %, based on the total weight of the composition.

Examples of suitable liquid carriers potentially useful in the present compositions include but are not limited to water; aromatic hydrocarbons such as alkylbenzenes and alkylnaphthalenes; alcohols such as methanol, cyclohexanol, and decanol; ethylene glycol; polypropylene glycol; dipropropylene glycol; N,N-dimethylformamide; dimethylsulfoxide; N-alkylpyrrolidones such as N-methyl-2-

pyrrolidone; paraffins; various oils such as olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed, or coconut oil; fatty acid esters; ketones such as cyclohexanone, 2-heptanone, isophorone, and 4-hydroxy-4-methyl-2-pentanone; and the like.

Examples of suitable solid carriers potentially useful in the present compositions include but are not limited to mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, sodium carbonate and bicarbonate, and sodium sulfate; ground synthetic materials; fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal, and nutshell meal; cellulose powders; and other solid carriers.

As used herein, the term "surfactant" refers to any agriculturally acceptable material which imparts emulsifiability, stability, spreading, wetting, dispersibility, or other surface-modifying properties. Examples of suitable surfactants include, but are not limited to, non-ionic, anionic, cationic and ampholytic types such as alkoxylated fatty alcohols, ethoxylated polysorbate (e.g. tween 20), ethoxylated castor oil, lignin sulfonates, fatty acid sulfonates (e.g. lauryl sulfonate), phosphate esters such as phosphate esters of alcohol alkoxylates, phosphate esters of alkylphenol alkoxylates and phosphate esters of styrylphenol ethoxylates, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, alkylarylsulfonates, ethoxylated alkylphenols and aryl phenols, polyalkylene glycols and sorbitol esters.

Other ingredients, such as wetting agents, anti-foaming, adhesives, neutralizers, thickeners, binders, sequestrates, fertilizers, or anti-freeze agents, may also be added to the present compositions.

Additionally, the present subject matter provides a method of controlling undesired vegetation comprising applying to a locus of the undesired vegetation a herbicidally effective amount of a mixture of an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof.

In an embodiment, the present subject matter provides a method of controlling undesired vegetation comprising applying to a locus of the undesired vegetation a

composition comprising an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, and/or a combination thereof; and at least one agriculturally acceptable carrier. In a specific embodiment, the Auxin type herbicide is fluroxypyr meptyl. In another specific embodiment, the bromoxynil is bromoxynil octanoate.

In a specific embodiment, the present subject matter relates to a method of controlling undesired vegetation comprising applying to a locus of the undesired vegetation a herbicidally effective amount of a mixture of fluroxypyr meptyl, bromoxynil octanoate and diflufenican.

In a specific embodiment, the present subject matter relates to a method of controlling undesired vegetation comprising applying to a locus of the undesired vegetation a herbicidally effective amount of a mixture of MCPA, bromoxynil octanoate and diflufenican.

The mixtures and the herbicidal compositions can be applied pre-plant incorporated, pre- or post-emergence.

As used in the present methods, the herbicidal compositions and herbicidal mixtures discussed herein may be applied jointly or in a succession. That is, any of the Auxin type herbicide, bromoxynil, and diflufenican may be applied jointly or in succession.

In an embodiment, the mixture is applied on crops which include one or more of cereals, wheat, winter wheat, spring wheat, barley, winter barley, spring barley, oats, triticale, cereal rye, winter durum wheat, winter oat, spring oat, fodder cereals, maize, and grassland. That is, the locus of undesired vegetation may contain one or more of these crops.

In yet another embodiment, the undesired vegetation may include one or more of *Brassica napus, Arctotheca calendula, Sinapis arvensis, Stellaria media, Sonchus oleraceus, Buglossoides arvense, Ipomoea lonchophylla, Crassula* spp., *Lamium amplexicaule, Fumaria densiflora, Rumex* spp., *Emex australis, Chenopodium album, Senecio* spp., *Fumaria* spp., *Sisymbrium officinale, Melilotus indicus Marrubium vulgare, Lythrum hyssopifolia, Mesembryanthemum* spp., *Sisymbrium orientale, Sisymbrium irio, Erodium botrys, Cerastium glomeratum, Matthiola longipetala, Echium plantagineum, Lepidium* spp., *Lactuca serriola, Scleroblitum atriplicinum,*

*Papaver hybridum*, *Carthamus lanatus*, *Anagallis arvensis*, *Capsella bursa-pastoris*, *Chondrilla juncea*, *Rumex* spp., *Onopordum acaulon*, *Juncus bufonius*, *Polygonum patulum*, *Rapistrum rugosum*, *Silybum marianum*, *Vicia sativa*, *Lupinus* spp., *Carrichtera annua*, *Raphanus raphanistrum*, *Brassica tournefortii*, *Polygonum aviculare*, *Malva parviflora*, *Solanum nigrum*, *Amaranthus retroflexus*, *Galium* spp., *Matricaria* spp., *Veronica* spp., *Papaver rhoeas*, *Viola arvensis*, *Geranium* spp., and *Myosotis arvensis*.

In a further embodiment, the undesired vegetation may include one or more of *Chenopodium album*, *Amaranthus retroflexus*, *Galium* spp., *Matricaria* spp., *Veronica* spp., *Papaver rhoeas*, *Viola arvensis*, *Geranium* spp., and *Myosotis arvensis*.

In an embodiment, the herbicidal mixture is applied to the locus of undesired vegetation in an amount, or at a rate of application, of from 0.01 to 100 liter/ha. In yet another embodiment, the herbicidal mixture is applied in an amount of from 0.1 to 10 liter/ha. In another embodiment, the herbicidal mixture is applied in an amount of from 0.1 to 1 liter/ha.

In a specific embodiment, the mixture is applied to the locus of undesired vegetation in an amount of 0.1 liter/ha. In yet another specific embodiment, the mixture is applied in an amount of 0.25 liter/ha. In still another specific embodiment, the mixture is applied in an amount of 0.5 liter/ha. In still yet another specific embodiment, the mixture is applied in an amount of 0.75 liter/ha. In a further specific embodiment, the mixture is applied in an amount of 2 liter/ha. In yet another specific embodiment, the mixture is applied in an amount of 1 liter/ha.

In another embodiment, the herbicidal mixture is applied to the locus of undesired vegetation in an amount of from 1 to 1000 g/ha. In a further embodiment, the herbicidal mixture is applied in an amount of from 100 to 600 g/ha.

In a specific embodiment, the mixture of fluroxypyr meptyl, bromoxynil octanoate, and diflufenican is applied to the locus of undesired vegetation in an amount of 590 g/ha. In yet another specific embodiment, the mixture of fluroxypyr meptyl, bromoxynil octanoate, and diflufenican is applied in an amount of 325 g/ha. In still yet another specific embodiment, the mixture of fluroxypyr meptyl, bromoxynil octanoate, and diflufenican is applied in an amount of 275 g/ha. In a further specific embodiment, the mixture of fluroxypyr meptyl, bromoxynil octanoate, and diflufenican is applied in

an amount of 250 g/ha. Correspondingly, the amount of diflufenican is between 50 g/ha to 75 g/ha, fluroxypyr meptyl is from 50 g/ha to 100 g/ha, and bromoxynil octanoate is 50 to 150 g/ha.

In an embodiment, the mixture of MCPA, bromoxynil octanoate, and diflufenican is applied to the locus of undesired vegetation in an amount of about 570 g/ha. In another embodiment, the mixture of MCPA, bromoxynil octanoate, and diflufenican is applied in an amount of about 522.5 g/ha. In yet another embodiment, the mixture of MCPA, bromoxynil octanoate, and diflufenican is applied in an amount of about 475 g/ha. In a further embodiment, the mixture of MCPA, bromoxynil octanoate, and diflufenican is applied in an amount of about 475 g/ha. Correspondingly, the amount of diflufenican is between about 20 g/ha to about 35 g/ha, MCPA is from about 150 g/ha to about 300 g/ha, and bromoxynil octanoate is about 100 to about 350 g/ha.

In another embodiment, the present subject matter provides a kit comprising the herbicidal mixture as described herein, or components thereof. Such kits may comprise, in addition to the aforementioned active components, one or more additional active and/or inactive ingredients, either within the provided herbicidal composition or separately. Certain kits comprise an Auxin type herbicide, bromoxynil and diflufenican, or an esters or salt of any of the foregoing, and/or a combination thereof, each in a separate container, and each optionally combined with a carrier.

In an embodiment, the kit comprises fluroxypyr meptyl, bromoxynil octanoate, and diflufenican. In another embodiment, the kit comprises MCPA, bromoxynil octanoate, and diflufenican.

A synergistic effect exists wherever the action of a combination of active components is greater than the sum of the action of each of the components alone. Therefore, a synergistically effective amount (or an effective amount of a synergistic composition or combination) as discussed herein is an amount that exhibits greater pesticidal activity than the sum of the pesticidal activities of the individual components.

In the context of the present subject matter, the term “synergy” is as defined by Colby S. R. in an article entitled "Calculation of the synergistic and antagonistic responses of herbicide combinations" published in the journal *Weeds*, 1967, 15, p. 20-

22, incorporated herein by reference in its entirety. The action expected for a given combination of three active components can be calculated as follows:

$$E = X + Y + Z - \frac{XY + XZ + YZ}{100} + \frac{XYZ}{10000}$$

in which E represents the expected percentage of pesticidal control for the combination of the three pesticides at defined doses (for example equal to x, y and z respectively), X is the percentage of herbicidal control observed by fluroxypyr meptyl at a defined dose (equal to x), Y is the percentage of herbicidal control observed by bromoxynil octanoate at a defined dose (equal to y), and Z is the percentage of herbicidal control of diflufenican at a defined dose (equal to z). When the percentage of herbicidal control observed for the combination is greater than the expected percentage, there is a synergistic effect. When the percentage of control observed for the combination is equal to the expected percentage, there is an additive effect and wherein the percentage of herbicidal control observed for the combination is lower than the expected percentage, there is an antagonistic effect.

EXPERIMENTAL DETAILS

The experiments were conducted by tank mixing bromoxynil octanoate, 225 g/L EC (commercially available Bromotril®), fluroxypyr meptyl, 200 g/L EC (commercially available Tomahawk®) and diflufenican, 500 g/L SC (commercially available Hurricane®) in different application rates.

Weed seeds were sown in 0.3 L pots containing Medium-heavy clay-loam soil from Newe Ya'ar Research Center fields (55% clay, 23% silt, 20% sand, 2% organic matter, pH 7.1).

The experiments were conducted in a completely randomized design. Each treatment was replicated 5 times. The herbicides were applied with a motorized sprayer equipped with a Tee Jet 8001E nozzle (Spraying Systems Co., North Ave., Wheaton, IL. 60188, USA) and operated at a pressure of 300 kPa. The pots were transferred to a net house 24 hours after the herbicide application and were sprinkler irrigated to field capacity of the soil. The plants were grown in the net house during the entire

experiment duration.

TABLE 1

The tested plant species and their condition at the time of herbicide application

| **Height cm** | **Leaves No.** | **Latin name** | **Common Name** |
|---|---|---|---|
| 2-6 | 2-6 | *Chenopodium album* | Lamb's quarters |
| 3-9 | 2-6 | *Amaranthus retroflexus* | Redroot pigweed |

5

The % control observed was calculated as follows:

$$\%\ \text{control observed} = \frac{\text{Mean weed count in untreated control} - \text{Mean weed count in treated plot}}{\text{Mean weed count in untreated control}} * 100$$

TABLE 2

Tank mix of Fluroxypyr meptyl + Bromoxynil octanoate + Diflufenican on *Chenopodium Album*

| | | % control observed | | | | % control expected | | | | Colby Ratio | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AI** | **Application rate (ml/ha)** | **6DAA** | **12DAA** | **19DAA** | **26DAA** | **6DAA** | **12DAA** | **19DAA** | **26DAA** | **6DAA** | **12DAA** | **19DAA** | **26DAA** |
| Diflufenican 500 SC | 100 | 5.00 | 10.00 | 0.00 | 0.00 | | | | | | | | |
| Fluroxypyr 200 EC | 250 | 10.00 | 10.00 | 20.00 | 10.00 | | | | | | | | |
| Fluroxypyr 200 EC | 500 | 30.00 | 35.00 | 40.00 | 30.00 | | | | | | | | |
| Bromoxynil 225 EC | 675 | 30.00 | 50.00 | 30.00 | 20.00 | | | | | | | | |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 100+250+675 | 70.00 | 95.00 | 95.00 | 95.00 | 40.15 | 59.50 | 44.00 | 28.00 | 1.74 | 1.60 | 2.16 | 3.39 |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 100+500+675 | 85.00 | 100.00 | 100.00 | 99.00 | 53.45 | 70.75 | 58.00 | 44.00 | 1.59 | 1.41 | 1.72 | 2.25 |
| Diflufenican 500 SC | 150 | 5.00 | 10.00 | 5.00 | 5.00 | | | | | | | | |
| Fluroxypyr 200 EC | 250 | 10.00 | 10.00 | 20.00 | 10.00 | | | | | | | | |
| Fluroxypyr 200 EC | 500 | 30.00 | 35.00 | 40.00 | 30.00 | | | | | | | | |
| Bromoxynil 225 EC | 675 | 30.00 | 50.00 | 30.00 | 20.00 | | | | | | | | |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 150+250+675 | 70.00 | 97.00 | 95.00 | 95.00 | 40.15 | 59.50 | 46.80 | 31.60 | 1.74 | 1.63 | 2.03 | 3.01 |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 150+500+675 | 85.00 | 100.00 | 100.00 | 100.00 | 53.45 | 70.75 | 60.10 | 46.80 | 1.59 | 1.41 | 1.66 | 2.14 |

As shown in Table 2, application of diflufenican 500 SC and bromoxynil 225 EC alone provided extremely weak control. The low rates did not cause any damage

and the highest rates of 150 and 675 mL $ha^{-1}$ were extremely weak. The formulation of fluroxypyr 200 EC alone showed higher control efficacy 24 hours after application but the plants recovered toward the end of the experiment. The lowest rate of 250 mL $ha^{-1}$ caused slight injuries and the rate of 500 mL $ha^{-1}$ was slightly more aggressive. However, the combination of all three components together at all rates completely controlled the weed.

TABLE 3

Tank mix of Fluroxypyr meptyl + Bromoxynil octanoate + Diflufenican on *Amaranthus retroflexus*

| | | % control observed | | | | % control expected | | | | Colby Ratio | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **AI** | **Application rate (ml/ha)** | **6DAA** | **12DAA** | **19DAA** | **26DAA** | **6DAA** | **12DAA** | **19DAA** | **26DAA** | **6DAA** | **12DAA** | **19DAA** | **26DAA** |
| Diflufenican 500 SC | 100 | 5.00 | 30.00 | 30.00 | 65.00 | | | | | | | | |
| Fluroxypyr 200 EC | 250 | 50.00 | 30.00 | 10.00 | 5.00 | | | | | | | | |
| Fluroxypyr 200 EC | 500 | 60.00 | 45.00 | 45.00 | 45.00 | | | | | | | | |
| Bromoxynil 225 EC | 675 | 5.00 | 10.00 | 0.00 | 0.00 | | | | | | | | |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 100+250+675 | 65.00 | 60.00 | 70.00 | 85.00 | 54.88 | 55.90 | 37.00 | 66.75 | 1.18 | 1.07 | 1.89 | 1.27 |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 100+500+675 | 60.00 | 70.00 | 90.00 | 100.00 | 63.90 | 65.35 | 61.50 | 80.75 | 0.94 | 1.07 | 1.46 | 1.24 |
| Diflufenican 500 SC | 150 | 5.00 | 30.00 | 30.00 | 65.00 | | | | | | | | |
| Fluroxypyr 200 EC | 250 | 50.00 | 30.00 | 10.00 | 5.00 | | | | | | | | |
| Fluroxypyr 200 EC | 500 | 60.00 | 45.00 | 45.00 | 45.00 | | | | | | | | |
| Bromoxynil 225 EC | 675 | 5.00 | 10.00 | 0.00 | 0.00 | | | | | | | | |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 150+250+675 | 65.00 | 60.00 | 90.00 | 99.00 | 54.88 | 55.90 | 37.00 | 66.75 | 1.18 | 1.07 | 2.43 | 1.48 |
| Diflufenican 500 SC + Fluroxypyr 200 EC + Bromoxynil 225 EC | 150+500+675 | 65.00 | 70.00 | 99.00 | 100.00 | 63.90 | 65.35 | 61.50 | 80.75 | 1.02 | 1.07 | 1.61 | 1.24 |

As shown in Table 3, application of bromoxynil 225 EC alone did not cause any damage to the weeds. Application of fluroxypyr 200 EC alone at a rate of 250 mL $ha^{-1}$ caused an initial intermediate damage but the plants recovered almost completely at the

end of the experiment. An administration rate of 500 mL $ha^{-1}$ had a similar effect but the plants had a lower recovery. Administration of diflufenican 500 SC alone at all rates had a pronounced herbicidal effect. However, the combination of all three components together at the rates of 675 + 100 + 250 mL $ha^{-1}$ was highly effective and at the higher rates of 675 + 100 + 500, 675 + 150 + 250, and 675 + 150 + 500 mL $ha^{-1}$ controlled the weed completely.

As can be seen from the calculated herbicide test results (Colby Ratio o/e) in Tables 2 and 3, the ternary mixture provided a greater herbicide effect than expected from their individual effects on *Chenopodium album* and *Amaranthus retroflexus*. The synergistic effect occurred over a range of bromoxynil application rates, diflufenican applications rates and fluroxypyr application rates.

While the present subject matter has been shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that many alternatives, modifications and variations may be made thereto without departing from the spirit and scope thereof. Accordingly, it is intended to embrace all such alternatives, modifications, and variations that fall within the spirit and broad scope of the appended claims.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference.

CLAIMS:

1. A synergistic herbicidal mixture comprising an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, or a combination thereof.

2. The synergistic herbicidal mixture of claim 1, wherein said Auxin type herbicide is selected from the group consisting of fluroxypyr, MCPA, 2,4 D, aminopyralid, clopyralid, picloram, triclopyr, esters thereof, salts thereof, and a combination thereof.

3. The synergistic herbicidal mixture of claim 1 or 2, wherein said Auxin type herbicide is fluroxypyr meptyl.

4. The synergistic herbicidal mixture of claim 1 or 2, wherein said Auxin type herbicide is MCPA.

5. The synergistic herbicidal mixture of any one of claims 1 to 4, wherein said bromoxynil is bromoxynil octanoate.

6. The synergistic herbicidal mixture of any one of claims 1 to 5, wherein the weight ratio of said diflufenican, and said Auxin type herbicide is from 1:30 to 30:1.

7. The synergistic herbicidal mixture of any one of claims 1 to 6, wherein the weight ratio of said bromoxynil, and said Auxin type herbicide is from is from 1:10 to 10:1.

8. The synergistic herbicidal mixture of any one of claims 1 to 7, wherein the weight ratio between diflufenican, bromoxynil octanoate and fluroxypyr meptyl is 1:3:2.

9. The synergistic herbicidal mixture of any one of claims 1 to 7, wherein the weight ratio between diflufenican, bromoxynil octanoate and MCPA is 1:6:10.

10. The synergistic herbicidal mixture of any one of claims 1 to 7, wherein the weight ratio between diflufenican, bromoxynil octanoate and MCPA is 1:10:8.

11. The synergistic herbicidal mixture of any one of claims 1 to 10, wherein the auxin type herbicide, bromoxynil, and diflufenican are applied jointly or in a succession.

12. The synergistic herbicidal mixture of any one of claims 1 to 11, wherein said mixture is used to provide a rate of application of from 0.1 to 10 liter/ha.

13. The synergistic herbicidal mixture of claim 12, wherein said mixture is used to provide a rate of application of 2 liter/ha.

14. A composition comprising a mixture of an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, or a combination thereof; and at least one agriculturally acceptable carrier.

15. The composition of claim 14, further comprising at least one surfactant, solid diluent, liquid diluent, or a combination thereof.

16. The composition of claim 14 or 15, wherein said Auxin type herbicide is selected from the group consisting of fluroxypyr, MCPA, 2,4 D, aminopyralid, clopyralid, picloram, triclopyr, esters thereof, salts thereof, and a combination thereof.

17. The composition of any one of claims 14 to 16, wherein said Auxin type herbicide is fluroxypyr meptyl.

18. The composition of any one of claims 14 to 16, wherein said Auxin type herbicide is MCPA.

19. The composition of any one of claims 14 to 18, wherein said bromoxynil is bromoxynil octanoate.

20. The composition of any one of claims 14 to 19, wherein the Auxin type herbicide, bromoxynil, and diflufenican are together present in a concentration of about 25% to about 80% by weight of the total weight of all components in the composition.

21. The composition of any one of claims 14 to 20, wherein the weight ratio of said diflufenican, and said Auxin type herbicide is from 1:30 to 30:1.

22. The composition of any one of claims 14 to 21, wherein the weight ratio of said bromoxynil, and said Auxin type herbicide is from is from 1:10 to 10:1.

23. The composition of any one of claims 14 to 22, wherein the weight ratio between diflufenican, bromoxynil octanoate and fluroxypyr meptyl is 1:3:2.

24. The composition of any one of claims 14 to 22, wherein the weight ratio between diflufenican, bromoxynil octanoate and MCPA is 1:6:10.

25. The composition of any one of claims 14 to 22, wherein the weight ratio between diflufenican, bromoxynil octanoate and MCPA is 1:10:8.

26. A method of controlling undesired vegetation comprising applying to a locus of the undesired vegetation a herbicidally effective amount of a mixture comprising an Auxin type herbicide, bromoxynil, and diflufenican, or an ester or salt of any of the foregoing, or a combination thereof.

27. The method of claim 26, wherein said Auxin type herbicide is selected from the group consisting of fluroxypyr, MCPA, 2,4 D, aminopyralid, clopyralid, picloram, triclopyr, esters thereof, salts thereof, and a combination thereof.

28. The method of claim 26 or 27, wherein said Auxin type herbicide is fluroxypyr meptyl.

29. The method of claim 26 or 27, wherein said Auxin type herbicide is MCPA.

30. The method of any one of claims 26 to 29, wherein said bromoxynil is bromoxynil octanoate.

31. The method of any one of claims 26 to 30, wherein said locus of the undesired vegetation contains a crop to be treated selected from the group consisting of cereals, wheat, winter wheat, spring wheat, barley, winter barley, spring barley, oats, triticale, cereal, rye, winter durum wheat, winter oat, spring oat, fodder cereals, maize, grassland, and combinations thereof.

32. The method of any one of claims 26-31, wherein the weight ratio of said diflufenican, and said Auxin type herbicide is from 1:30 to 30:1.

33. The method of any one of claims 26-32 wherein the weight ratio of said bromoxynil, and said Auxin type herbicide is from is from 1:10 to 10:1.

34. The method of any one of claims 26-33, wherein the weight ratio between diflufenican, bromoxynil octanoate and fluroxypyr meptyl is 1:3:2.

35. The method of any one of claims 26-33, wherein the weight ratio between diflufenican, bromoxynil octanoate and MCPA is 1:6:10.

36. The method of any one of claims 26-33, wherein the weight ratio between diflufenican, bromoxynil octanoate and MCPA is 1:10:8.

37. The method of any one of claims 26 to 36, wherein the auxin type herbicide, bromoxynil, and diflufenican are applied jointly or in a succession.

38. The method of any one of claims 26 to 37, wherein the mixture is applied in an amount of from 100 to 600 g/ha.

39. The method of any one of claims 26-37, wherein said mixture is used to provide a rate of application of from 0.1 to 10 liter/ha.

40. The method of claim 39, wherein said mixture is used to provide a rate of application of 2 liter/ha.

41. A method of controlling undesired vegetation comprising applying to a locus of the undesired vegetation the composition of any one of claims 14 to 25.

42. The method of claim 41, wherein the composition is applied in an amount of from 100 to 600 g/ha.

43. The method of claim 41 or 42, wherein said composition is used to provide a rate of application of from 0.1 to 10 liter/ha.

44. The method of claim 43, wherein said composition is used to provide a rate of application of 2 liter/ha.

45. A kit comprising the herbicidal mixture according to any one of claims 1-13.

46. A kit comprising the composition according to any one of claims 14-25.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2014/050713

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N43/40 A01N37/40 A01P13/00
ADD.

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 2 December 2014 | 09/12/2014 |

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|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Bueno Torres, Pilar |

2

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