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(54) Title: SYNERGISTIC WEED CONTROL FROM APPLICATIONS OF AMINOPYRALID AND CLOPYRALID

(57) Abstract: Disclosed herein are herbicidal compositions comprising a synergistically herbicidal effective amount of (a) aminopyralid, or an agriculturally acceptable salt or ester thereof, and (b) clopyralid, or an agriculturally acceptable salt or ester thereof. Also disclosed herein are methods of controlling undesirable vegetation, which comprise applying to vegetation or an area adjacent the vegetation or applying to soil or water to prevent the emergence or growth of vegetation (a) aminopyralid, or an agriculturally acceptable salt or ester thereof, and (b) clopyralid, or an agriculturally acceptable salt or ester thereof, wherein (a) and (b) are each added in an amount sufficient to produce a synergistic herbicidal effect.



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## **SYNERGISTIC WEED CONTROL FROM APPLICATIONS OF AMINOPYRALID AND CLOPYRALID**

### **FIELD OF THE DISCLOSURE**

The present disclosure relates to herbicidal compositions comprising a synergistically herbicidal effective amount of (a) aminopyralid or an agriculturally acceptable salt or ester thereof, and (b) clopyralid or an agriculturally acceptable salt or ester thereof. The present disclosure also relates to methods for controlling undesirable vegetation.

### **BACKGROUND**

Many recurring problems in agriculture involve controlling growth of undesirable vegetation that can, for instance, inhibit crop growth. To help control undesirable vegetation, researchers have produced a variety of chemicals and chemical formulations effective in controlling such unwanted growth. However, a continuing need exists for new compositions and methods to control growth of undesirable vegetation.

### **SUMMARY OF THE DISCLOSURE**

Herbicides of many types have been disclosed in the literature and a number are in commercial use. In some cases, herbicidal active ingredients have been found more effective in combination than when applied individually and this is referred to as “synergy” or “synergism.” The present disclosure is based on the discovery that (a) aminopyralid, or an agriculturally acceptable salt or ester thereof, and (b) clopyralid, or an agriculturally acceptable salt or ester thereof, display a synergistic herbicidal effect when applied in combination.

Accordingly, the present disclosure relates to herbicidal compositions comprising a synergistically herbicidal effective amount of (a) aminopyralid, or an agriculturally acceptable salt or ester thereof, and (b) clopyralid, or an agriculturally acceptable salt or ester thereof. In some embodiments, (a) includes the aminopyralid triisopropanolamine salt. In some embodiments, (b) includes clopyralid monoethanolamine salt. The acid equivalent weight ratio of (a) to (b) can be less from 1:373 to 24:1 (e.g., from 1:5 to 2:1). In some embodiments, the composition further comprises an additional pesticide (e.g., aminocyclopyrachlor, amicarbazone, 4-aminopicolinic acids, bromoxynil, chlorsulfuron, 2,4-D, dicamba, dichlorprop-P, diclosulam, diuron, florasulam, flucarbazone-sodium, flumetsulam, fluroxypyr, glyphosate, glufosinate, imazamox, imazapyr, imazapic,

imazaquin, imazethapyr, imazamethabenz, indaziflam, ioxynil, MCPA, mecoprop-P, metsulfuron-methyl, oxyfluorfen, penoxsulam, picloram, pinoxaden, pyroxsulam, rimsulfuron, sulfmeturon, thifensulfuron-methyl, tebuthiuron, tribenuron-methyl, triclopyr, and agriculturally acceptable salts or esters or mixtures thereof). The additional pesticide can include 2,4-D choline salt, aminocyclopyrachlor choline salt, triclopyr choline salt, or a mixture thereof. In some embodiments, the composition is free of naptalam and salts and esters thereof. In some embodiments, the composition further comprises a herbicidal safener, an agriculturally acceptable adjuvant or carrier, or a combination thereof.

The present disclosure also relates to methods of controlling undesirable vegetation, which comprise applying to vegetation or an area adjacent the vegetation or applying to soil or water to prevent the emergence or growth of vegetation (a) aminopyralid, or an agriculturally acceptable salt or ester thereof and (b) clopyralid, or an agriculturally acceptable salt or ester thereof, wherein (a) and (b) are each added in an amount sufficient to produce a synergistic herbicidal effect. In some embodiments, (a) and (b) are applied simultaneously. In some embodiments, (a) and (b) are applied postemergence to the undesirable vegetation. The undesirable vegetation can be controlled in, for instance, CRP, fallow land, rangelands, pasture, IVM, or tree and vine. In some embodiments, the undesirable vegetation is honey mesquite. In some embodiments, the undesirable vegetation is resistant to auxinic herbicides. In some embodiments, (a) is applied in an amount of from 3–480 grams of acid equivalent per hectare (g ae/ha). In some embodiments, (b) is applied in an amount of from 20–1120 g ae/ha.

The description below sets forth details of one or more embodiments of the present disclosure. Other features, objects, and advantages will be apparent from the description and from the claims.

## DETAILED DESCRIPTION

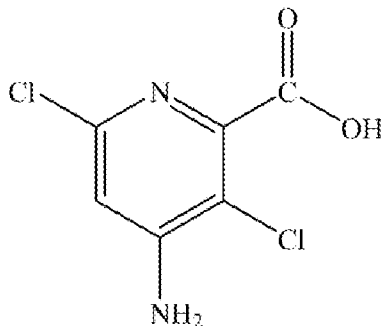
The present disclosure relates to herbicidal compositions comprising a synergistically herbicidal effective amount of (a) aminopyralid, or an agriculturally acceptable salt or ester thereof, and (b) clopyralid, or an agriculturally acceptable salt or ester thereof. The present disclosure also relates to methods for controlling undesirable vegetation.

The term “herbicide,” as used herein, means an active ingredient that kills, controls, or otherwise adversely modifies the growth of vegetation. A “herbicidally effective amount” is an amount of an active ingredient that causes a “herbicidal effect,” i.e., an adversely modifying effect and includes deviations from, for instance, natural development, killing,

regulation, desiccation, and retardation. The terms “plants” and “vegetation” can include, for instance, germinant seeds, emerging seedlings, and established vegetation.

### Aminopyralid

Compositions and methods of the present disclosure can include aminopyralid or an agriculturally acceptable salt or ester thereof. Aminopyralid (i.e., 4-amino-3,6-dichloro-2-pyridinecarboxylic acid), shown below, is a herbicide that can be used to control broadleaf weeds in, for instance, industrial vegetation, rangeland, and pastures. Its herbicidal activity is described in THE PESTICIDE MANUAL, Fifteenth Edition, 2009.



Aminopyralid can be provided in its acid form (as shown above), or as an agriculturally acceptable salt or ester thereof. Exemplary agriculturally acceptable salts or esters of aminopyralid include, but are not limited to, sodium salts, potassium salts, ammonium salts or substituted ammonium salts, in particular mono-, di- and tri- $C_1$ - $C_8$  -alkylammonium salts such as methyl ammonium, dimethylammonium and isopropylammonium (e.g., triisopropanolammonium), mono-, di- and tri-hydroxy- $C_2$  - $C_8$  -alkylammonium salts such as hydroxyethylammonium, di(hydroxyethyl)ammonium, tri(hydroxyethyl)ammonium, hydroxypropylammonium, di(hydroxypropyl)ammonium and tri(hydroxypropyl)ammonium salts, their diglycolamine salts and their esters, in particular its  $C_1$ - $C_8$  -alkyl esters and  $C_1$  - $C_4$  -alkoxy - $C_2$ - $C_4$  -alkyl esters, such as methyl esters, ethyl esters, isopropyl, butyl, hexyl, heptyl, isoheptyl, isooctyl, 2-ethylhexyl and butoxyethyl esters. Exemplary agriculturally acceptable salts or esters of aminopyralid can include aminopyralid-potassium, aminopyralid-olamine, aminopyralid-tris(2-hydroxypropyl) ammonium, aminopyralid-methyl, aminopyralid choline salt, and mixtures thereof. In some embodiments, the aminopyralid is provided as an amine salt, such as aminopyralid-olamine salt, dimethylamine (DMA) salt, monoethanolamine (MEA) salt, triisopropanolamine (TIPA) salt, or a mixture thereof. Aminopyralid and agriculturally acceptable salts or esters

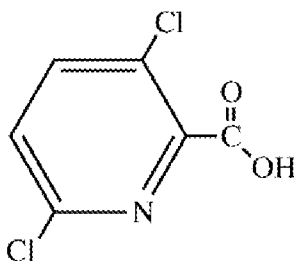
thereof are or have been commercially available, for example, under the trademark MILESTONE® (by DOW AGROSCIENCES LLC).

The aminopyralid or an agriculturally acceptable salt or ester thereof described herein can be used in an amount sufficient to induce a herbicidal effect. In some embodiments, the aminopyralid or agriculturally acceptable salt or ester thereof is applied to vegetation or an area adjacent the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of 3 grams of acid equivalent per hectare (g ae/ha) or greater (e.g., 10 g ae/ha or greater, 20 g ae/ha or greater, 30 g ae/ha or greater, 40 g ae/ha or greater, 50 g ae/ha or greater, 60 g ae/ha or greater, 70 g ae/ha or greater, 80 g ae/ha or greater, 90 g ae/ha or greater, 100 g ae/ha or greater, 120 g ae/ha or greater, 140 g ae/ha or greater, 160 g ae/ha or greater, 180 g ae/ha or greater, 200 g ae/ha or greater, 220 g ae/ha or greater, 240 g ae/ha or greater, 260 g ae/ha or greater, 280 g ae/ha or greater, 300 g ae/ha or greater, 320 g ae/ha or greater, 340 g ae/ha or greater, 360 g ae/ha or greater, 380 g ae/ha or greater, 400 g ae/ha or greater, 420 g ae/ha or greater, 440 g ae/ha or greater, or 460 g ae/ha or greater). In some embodiments, the aminopyralid or agriculturally acceptable salt or ester thereof is applied to vegetation or an area adjacent the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of 480 g ae/ha or less (e.g., 460 g ae/ha or less, 440 g ae/ha or less, 420 g ae/ha or less, 400 g ae/ha or less, 380 g ae/ha or less, 360 g ae/ha or less, 340 g ae/ha or less, 320 g ae/ha or less, 300 g ae/ha or less, 280 g ae/ha or less, 270 g ae/ha or less, 260 g ae/ha or less, 250 g ae/ha or less, 230 g ae/ha or less, 210 g ae/ha or less, 190 g ae/ha or less, 170 g ae/ha or less, 150 g ae/ha or less, 130 g ae/ha or less, 110 g ae/ha or less, 90 g ae/ha or less, 70 g ae/ha or less, 50 g ae/ha or less, 30 g ae/ha or less, 25 g ae/ha or less, 20 g ae/ha or less, 15 g ae/ha or less, or 10 g ae/ha or less). In some embodiments, the aminopyralid or agriculturally acceptable salt or ester thereof is applied to vegetation or an area adjacent the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of from 3–480 g ae/ha (e.g., from 25–440 g ae/ha, from 50–400 g ae/ha, from 75–350 g ae/ha, from 100–300 g ae/ha, from 125–250 g ae/ha, from 150–200 g ae/ha).

### **Clopyralid**

Compositions and methods of the present disclosure can include clopyralid or an agriculturally acceptable salt or ester thereof. Clopyralid (i.e., 3,6-dichloropicolinic acid; 3,6-dichloro-2-pyridinecarboxylic acid), shown below, is a herbicide that can be used to control broadleaf weeds in, for instance, cereal crops, ornamentals, pastures, fallow, turf,

rangelands, forest, and industrial applications. Its herbicidal activity is described in The Pesticide Manual, Fifteenth Edition, 2009.



Clopyralid can be provided in its acid form (as shown above), or as an agriculturally acceptable salt or ester thereof. Exemplary agriculturally acceptable salts or esters of clopyralid include, but are not limited to, sodium salts, potassium salts, ammonium salts or substituted ammonium salts, in particular mono-, di- and tri- $C_1$ - $C_8$  -alkylammonium salts such as methyl ammonium, dimethylammonium and isopropylammonium, mono-, di- and tri-hydroxy- $C_2$  - $C_8$  -alkylammonium salts such as hydroxyethylammonium, di(hydroxyethyl)ammonium, tri(hydroxyethyl)ammonium, hydroxypropylammonium, di(hydroxypropyl)ammonium and tri(hydroxypropyl)ammonium salts, their diglycolamine salts and their esters, in particular its  $C_1$ - $C_8$  -alkyl esters and  $C_1$  - $C_4$  -alkoxy - $C_2$ - $C_4$  -alkyl esters, such as methyl esters, ethyl esters, isopropyl, butyl, hexyl, heptyl, isoheptyl, iso-octyl, 2-ethylhexyl and butoxyethyl esters; and aryl esters such as benzyl. Exemplary agriculturally acceptable salts or esters of clopyralid can include clopyralid-potassium, clopyralid-olamine, clopyralid-tris(2-hydroxypropyl) ammonium, clopyralid-methyl, and mixtures thereof. In some embodiments, the clopyralid is provided as an amine salt, such as clopyralid-olamine salt, dimethylamine (DMA) salt, monoethanolamine (MEA) salt, triisopropanolamine (TIPA) salt, or a mixture thereof. Clopyralid and agriculturally acceptable salts or esters thereof are or have been commercially available, for example, under the trademarks LONTREL® (by DOW AGROSCIENCES LLC), RECLAIM® (by DOW AGROSCIENCES LLC), DOW SHIELD® (by DOW AGROSCIENCES LLC), STINGER® (by DOW AGROSCIENCES LLC), TRANSLINE® (by DOW AGROSCIENCES LLC), FETREL® (by FERTIAGRO PTE. LTD.), CLEAN SLATE® (by NUFARM AMERICAS INC.), GARRISON® (by NUFARM AMERICAS INC.), PHAETON® (by HEKTAS TICARET T.A.S.), CLOPYR® (by UNITED PHOSPHOROUS LTD.), CLEO® (by PARIJAT), WOPRO-CLOPYRALID® (by B.V. INDUSTRIE- & HANDELSONDERNEMING SIMONIS), BOSS® (by STOCKTON AGRIMOR AG), PIRATE® (by WILLOWOOD LTD.), TRELAN® (by WILLOWOOD LTD.), and TANGO® (by ZELAM LTD.).

The clopyralid or an agriculturally acceptable salt or ester thereof described herein can be used in an amount sufficient to induce a herbicidal effect. In some embodiments, the clopyralid or agriculturally acceptable salt or ester thereof is applied to vegetation or an area adjacent the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of 20 grams or greater of acid equivalent per hectare (g ae/ha) (e.g., 30 g ae/ha or greater, 40 g ae/ha or greater, 50 g ae/ha or greater, 60 g ae/ha or greater, 70 g ae/ha or greater, 80 g ae/ha or greater, 90 g ae/ha or greater, 100 g ae/ha or greater, 110 g ae/ha or greater, 120 g ae/ha or greater, 130 g ae/ha or greater, 140 g ae/ha or greater, 160 g ae/ha or greater, 180 g ae/ha or greater, 200 g ae/ha or greater, 250 g ae/ha or greater, 300 g ae/ha or greater, 350 g ae/ha or greater, 400 g ae/ha or greater, 450 g ae/ha or greater, 500 g ae/ha or greater, 550 g ae/ha or greater, 600 g ae/ha or greater, 650 g ae/ha or greater, 700 g ae/ha or greater, 750 g ae/ha or greater, 800 g ae/ha or greater, 850 g ae/ha or greater, 900 g ae/ha or greater, 950 g ae/ha or greater, 1000 g ae/ha or greater, or 1050 g ae/ha or greater). In some embodiments, the clopyralid or agriculturally acceptable salt or ester thereof is applied to vegetation or an area adjacent the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of 1120 g ae/ha or less (e.g., 1100 g ae/ha or less, 1050 g ae/ha or less, 1000 g ae/ha or less, 950 g ae/ha or less, 900 g ae/ha or less, 850 g ae/ha or less, 800 g ae/ha or less, 750 g ae/ha or less, 700 g ae/ha or less, 650 g ae/ha or less, 600 g ae/ha or less, 550 g ae/ha or less, 500 g ae/ha or less, 450 g ae/ha or less, 400 g ae/ha or less, 380 g ae/ha or less, 360 g ae/ha or less, 340 g ae/ha or less, 320 g ae/ha or less, 300 g ae/ha or less, 280 g ae/ha or less, 270 g ae/ha or less, 260 g ae/ha or less, 250 g ae/ha or less, 240 g ae/ha or less, 230 g ae/ha or less, 220 g ae/ha or less, 210 g ae/ha or less, 200 g ae/ha or less, 190 g ae/ha or less, 180 g ae/ha or less, 170 g ae/ha or less, 160 g ae/ha or less, 150 g ae/ha or less, 140 g ae/ha or less, 130 g ae/ha or less, 120 g ae/ha or less, 110 g ae/ha or less, 100 g ae/ha or less, 90 g ae/ha or less, 80 g ae/ha or less, 70 g ae/ha or less, 60 g ae/ha or less, 50 g ae/ha or less, 40 g ae/ha or less, or 30 g ae/ha or less). In some embodiments, the clopyralid or agriculturally acceptable salt or ester thereof is applied to vegetation or an area adjacent the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of from 20–1120 g ae/ha (e.g., from 22–800 g ae/ha, from 23–500 g ae/ha, from 25–250 g ae/ha, from 30–200 g ae/ha, from 35–175 g ae/ha, from 40–150 g ae/ha, from 45–125 g ae/ha, from 50–110 g ae/ha, 70–100 g ae/ha, or from 85–95 g ae/ha).

### **Herbicidal Mixtures or Combinations**

The (a) aminopyralid or an agriculturally acceptable salt or ester thereof is mixed with or applied in combination with (b) clopyralid or an agriculturally acceptable salt or ester thereof in an amount sufficient to induce a synergistic herbicidal effect. In some embodiments, (a) and (b) are used in an amount sufficient to induce a synergistic herbicidal effect while still showing good crop compatibility (i.e. their use in crops does not result in increased damage to crops when compared to the individual application of the herbicidal compounds (a) or (b)). As described in the *Herbicide Handbook* of the Weed Science Society of America, Ninth Edition, 2007, p. 429, “‘synergism’ [is] an interaction of two or more factors such that the effect when combined is greater than the predicted effect based on the response to each factor applied separately.” Synergistic in the herbicide context can mean that the use of (a) and (b) as defined above results in an increased weed control effect compared to the weed control effects that are possible with the use of (a) or (b) alone. In some embodiments, the damage or injury to the undesired vegetation caused by the compositions and methods disclosed herein is evaluated using a scale from 0% to 100%, when compared with the untreated control vegetation, wherein 0% indicates no damage to the undesired vegetation and 100% indicates complete destruction of the undesired vegetation. In some embodiments, Colby’s formula is applied to determine whether using (a) and (b) in combination shows a synergistic effect: S. R. Colby, *Calculating Synergistic and Antagonistic Responses of Herbicide Combinations*, WEEDS 15, p. 22 (1967)

$$E = X + Y - \frac{X \cdot Y}{100}$$

wherein

X=effect in percent using (a) aminopyralid or an agriculturally acceptable salt or ester thereof at an application rate *a*;

Y=effect in percent using (b) clopyralid or an agriculturally acceptable salt or ester thereof at an application rate *b*;

E=expected effect (in %) of (a)+(b) at application rates *a* and *b*.

In Colby’s equation, the value E corresponds to the effect (plant damage or injury) that is to be expected if the activity of the individual compounds is additive. If the observed effect is higher than the value E calculated according to the Colby equation, then a synergistic effect is present according to the Colby equation.

In some embodiments, the compositions and methods disclosed herein are synergistic as defined by the Colby equation. In some embodiments, the joint action of

aminopyralid or an agriculturally acceptable salt or ester thereof and clopyralid or an agriculturally acceptable salt or ester thereof results in enhanced activity against undesired vegetation (via synergism), even at application rates below those typically used for the pesticide to have a herbicidal effect on its own. In some embodiments, the compositions and methods disclosed herein can, based on the individual components, be used at lower application rates to achieve a herbicidal effect comparable to the effect produced by the individual components at normal application rates. In some embodiments, the compositions and methods disclosed herein provide an accelerated action on undesired vegetation (i.e. they effect damaging of undesired vegetation more quickly compared with application of the individual herbicides).

In some embodiments, the acid equivalent weight ratio of (a) aminopyralid or agriculturally acceptable salt or ester thereof to (b) clopyralid or an agriculturally acceptable salt or ester thereof that is sufficient to induce a synergistic herbicidal effect is at least 1:373 (e.g., at least 1:350, at least 1:300, at least 1:275, at least 1:250, at least 1:240, at least 1:230, at least 1:220, at least 1:210, at least 1:200, at least 1:190, at least 1:180, at least 1:170, at least 1:160, at least 1:150, at least 1:140, at least 1:130, at least 1:120, at least 1:110, at least 1:100, at least 1:95, at least 1:90, at least 1:85, at least 1:80, at least 1:70, at least 1:60, at least 1:50, at least 1:40, at least 1:30, at least 1:20, at least 1:10, at least 1:9, at least 1:8, at least 1:7, at least 1:6, at least 1:5, at least 1:4, at least 1:3, at least 1:2, at least 1:1, at least 2:1, at least 3:1, at least 4:1, at least 5:1, at least 6:1, at least 7:1, at least 8:1, at least 9:1, at least 10:1, or at least 11:1). In some embodiments, the acid equivalent weight ratio of (a) to (b) that is sufficient to induce a synergistic herbicidal effect is 24:1 or less (e.g., 22:1 or less, 20:1 or less, 18:1 or less, 16:1 or less, 15:1 or less, 14:1 or less, 13:1 or less, 12:1 or less, 11:1 or less, 10:1 or less, 9:1 or less, 8:1 or less, 7:1 or less, 6:1 or less, 5:1 or less, 4:1 or less, 3:1 or less, 2:1 or less, 1:1 or less, 1:2 or less, 1:3 or less, 1:4 or less, 1:5 or less, 1:6 or less, 1:7 or less, 1:8 or less, 1:9 or less, 1:10 or less, 1:15 or less, 1:30 or less, 1:45 or less, 1:60 or less, 1:75 or less, or 1:90 or less). In some embodiments, the acid equivalent weight ratio of (a) to (b) is from 1:373 to 24:1 (e.g., from 1:100 to 12:1, from 1:80 to 11:1, from 1:60 to 9:1, from 1:40 to 7:1, from 1:20 to 5:1, from 1:10 to 3:1, from 1:5 to 2:1, or from 1:1 to 2:1).

### **Formulations**

The present disclosure also relates to formulations of the compositions and methods disclosed herein. In some embodiments, the formulation can be in the form of a single

package formulation including both (a) aminopyralid or an agriculturally acceptable salt or ester thereof and (b) clopyralid or an agriculturally acceptable salt or ester thereof. In some embodiments, the formulation can be in the form of a single package formulation including both (a) and (b) and further including at least one additive. In some embodiments, the formulation can be in the form of a two-package formulation, wherein one package contains (a) and optionally at least one additive while the other package contains (b) and optionally at least one additive. In some embodiments of the two-package formulation, the formulation including (a) and optionally at least one additive and the formulation including (b) and optionally at least one additive are mixed before application and then applied simultaneously. In some embodiments, the mixing is performed as a tank mix (i.e., the formulations are mixed immediately before or upon dilution with water). In some embodiments, the formulation including (a) and the formulation including (b) are not mixed but are applied sequentially (in succession), for example, immediately or within 1 hour, within 2 hours, within 4 hours, within 8 hours, within 16 hours, within 24 hours, within 2 days, or within 3 days, of each other.

In some embodiments, the formulation of (a) and (b) is present in suspended, emulsified, or dissolved form. Exemplary formulations include, but are not limited to, aqueous solutions, powders, suspensions, also highly-concentrated aqueous, oily or other suspensions or dispersions, aqueous emulsions, aqueous microemulsions, aqueous suspo-emulsions, oil dispersions, pastes, dusts, and materials for spreading or granules.

In some embodiments, (a) aminopyralid or an agriculturally acceptable salt or ester thereof and/or (b) clopyralid or an agriculturally acceptable salt or ester thereof is an aqueous solution that can be diluted before use. In some embodiments, (a) and/or (b) is provided as a high-strength formulation such as a concentrate. In some embodiments, the concentrate is stable and retains potency during storage and shipping. In some embodiments, the concentrate is a clear, homogeneous liquid that is stable at temperatures of 54°C or greater. In some embodiments, the concentrate does not exhibit any precipitation of solids at temperatures of -10°C or higher. In some embodiments, the concentrate does not exhibit separation, precipitation, or crystallization of any components at low temperatures. For example, the concentrate remains a clear solution at temperatures below 0°C (e.g., below -5°C, below -10°C, below -15°C). In some embodiments, the concentrate exhibits a viscosity of less than 50 centipoise (50 megapascals), even at temperatures as low as 5°C.

The compositions and methods disclosed herein can also be mixed with or applied with an additive. In some embodiments, the additive can be diluted in water or can be

concentrated. In some embodiments, the additive is added sequentially. In some embodiments, the additive is added simultaneously. In some embodiments, the additive is premixed with the aminopyralid or agriculturally acceptable salt or ester thereof. In some embodiments, the additive is premixed with the clopyralid or agriculturally acceptable salt or ester thereof. In some embodiments, the additive is premixed with the aminopyralid or agriculturally acceptable salt or ester and the clopyralid or agriculturally acceptable salt or ester thereof.

In some embodiments, the additive is an additional pesticide. Exemplary additional pesticides include, but are not limited to, 2,4-D, aminocyclopyrachlor, acetochlor, aclonifen, amicarbazone, 4-aminopicolinic acid based herbicides, such as halauxifen, halauxifen-methyl, and those described in U.S. Patent Nos. 7,314,849 (B2) and 7,432,227 (B2), amidosulfuron, aminopyralid, aminotriazole, ammonium thiocyanate, asulam, atrazine, beflubutamid, benazolin, bentazone, bifenox, bromacil, bromoxynil, butachlor, butafenacil, butralin, butoxydim, carbetamide, carfentrazone, carfentrazone-ethyl, chlormequat, chlorsulfuron, chlortoluron, cinidon-ethyl, clethodim, clodinafop-propargyl, clomazone, cyanazine, cyclosulfamuron, cycloxydim, dicamba, dichlobenil, dichlorprop-P, diclofop-methyl, diclosulam, diflufenican, diflufenzopyr, dimefuron, dimethachlor, diquat, diuron, EPTC, ET-7 51, ethoxysulfuron, fenoxaprop, fenoxaprop-ethyl, fenoxaprop-ethyl+isoxidifen-ethyl, fenoxaprop-p-ethyl, fenoxasulfone, flazasulfuron, florasulam, fluazifop, fluazifop-P-butyl, flucarbazone, flucabazone-sodium, flucetosulfuron (LGC-42153), flufenacet, flumetsulam, flumioxacin, flupyrsulfuron, fluroxypyr, fluroxypyr-meptyl, flurtamone, glufosinate, glufosinate-ammonium, glyphosate, haloxyfop-methyl, haloxyfop-R, hexazinone, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, indanofan, indaziflam, iodosulfuron, iodosulfuron-ethyl-sodium, ioxynil, isoproturon, isoxaben, isoxaflutole, KIH-845, lactofen, linuron, MCPA, MCPB, mecoprop-P, mesosulfuron, mesosulfuron-ethyl sodium, metazochlor, metosulam, metribuzin, metsulfuron, metsulfuron-methyl, MSMA, napropamide, norfurazon, orthosulfamuron, oryzalin, oxadiargyl, oxadiazon, oxyfluorfen, paraquat, pendimethalin, penoxsulam, picloram, picolinafen, pinoxaden, primisulfuron, proflunazone, propaquizafop, propoxycarbazine, propyzamide, prosulfocarb, prosulfuron, pyraflufen ethyl, pyrasulfotole, pyribenzoxim (LGC-40863), pyroxsulam, pyroxsulfone, quinmerac, quizalofop-ethyl-D, quizalofop-P-ethyl, quizalofop-p-tefuryl, rimsulfuron, sethoxydim, simazine, sulfentrazone, sulfometuron, sulfosate, sulfosulfuron, tebuthiuron, tepraloxim, terbacil, terbutryn, thiazopyr, thifensulfuron, thifensulfuron-methyl, topramezone, tralkoxydim, triasulfuron,

tribenuron, tribenuron-methyl, triafamone, triclopyr, and trifluralin, and agriculturally acceptable salts, esters and mixtures thereof. In some embodiments, the additional pesticide includes 2,4-D choline salt, triclopyr choline salt, aminocyclopyrachlor choline salt, or a mixture thereof.

In some embodiments, the compositions and methods disclosed herein do not incorporate naptalam (i.e., N-1-naphthylphthalamic acid or NPA) or the salts or esters thereof. In some embodiments, the compositions and methods disclosed herein are free of naptalam or the salts or esters thereof. In some embodiments, naptalam or the salts or esters thereof are not applied to the vegetation, the area adjacent to the vegetation, the soil, or the water, in the methods disclosed herein.

In some embodiments, the aminopyralid or an agriculturally acceptable salt or ester thereof is provided in a premixed formulation with an additional pesticide. In some embodiments, the aminopyralid or an agriculturally acceptable salt or ester thereof is premixed with clopyralid, fluroxypyr, metsulfuron-methyl, 2,4-D, or mixtures thereof. Exemplary premixes of aminopyralid or an agriculturally acceptable salt or ester thereof and an additive that are or have been commercially available include, but are not limited to, SENDERO® (a premix incorporating clopyralid by DOW AGROSCIENCES LLC), CAPSTONE® (a premix incorporating triclopyr by DOW AGROSCIENCES LLC), CLEANWAVE® (a premix incorporating fluroxypyr by DOW AGROSCIENCES LLC), CHAPARRAL® and OPENSIGHT® (a premix incorporating metsulfuron-methyl by DOW AGROSCIENCES LLC), CLEARVIEW® (a premix incorporating metsulfuron-methyl by DOW AGROSCIENCES LLC), FOREFRONT® R&P and FOREFRONT® HL (a co-pack product incorporating 2,4-D by DOW AGROSCIENCES LLC), GRAZONNEXT® and GRAZONNEXT® HL (a co-pack product incorporating 2,4-D by DOW AGROSCIENCES LLC), PASTURALL® (a co-pack product incorporating 2,4-D by DOW AGROSCIENCES LLC), and RESTORE® (a co-pack product incorporating 2,4-D by DOW AGROSCIENCES LLC).

In some embodiments, the clopyralid or an agriculturally acceptable salt or ester thereof is provided in a premixed formulation with an additional pesticide. In some embodiments, the clopyralid or an agriculturally acceptable salt or ester thereof is premixed with acetochlor, benazolin, bensulfuron-methyl, 2,4-D, dicamba, flumetsulam, fluroxypyr, glufosinate, glyphosate, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, MCPA, triclopyr, or mixtures thereof. Exemplary premixes of clopyralid or an agriculturally acceptable salt or ester thereof and an additive that are or

have been commercially available include, but are not limited to, CURTAIL® (a premix incorporating 2,4-D by DOW AGROSCIENCES LLC), MILLENIUM ULTRA 2 ® (a premix incorporating 2,4-D and dicamba by NUFARM AMERICAS INC.), SURESTART® (a premix incorporating acetochlor and flumetsulam by DOW AGROSCIENCES LLC), BENAZALOX® (a premix incorporating benazolin by BAYER CROPSCIENCE), KE CAOTE® (a premix incorporating bensulfuron –methyl by NANJING RED SUN CO., LTD.), HORNET® (a premix incorporating flumetsulam by DOW AGROSCIENCES LLC), WIDEMATCH® (a premix incorporating fluroxypyr by DOW AGROSCIENCES LLC), HAT TRICK® (a premix incorporating fluroxypyr and MCPA by LOVELAND PRODS., INC.), CURTAIL M® (a premix incorporating MCPA by DOW AGROSCIENCES LLC), CONFRONT® (a premix incorporating triclopyr by DOW AGROSCIENCES LLC), and REDEEM® (a premix incorporating triclopyr by DOW AGROSCIENCES LLC).

In some embodiments, the additive includes an agriculturally acceptable adjuvant. Exemplary agriculturally acceptable adjuvants include, but are not limited to, antifreeze agents, antifoam agents, compatibilizing agents, sequestering agents, neutralizing agents and buffers, corrosion inhibitors, colorants, odorants, penetration aids, wetting agents, spreading agents, dispersing agents, thickening agents, freeze point depressants, antimicrobial agents, crop oil, safeners, adhesives (for instance, for use in seed formulations), surfactants, protective colloids, emulsifiers, tackifiers, and mixtures thereof. Exemplary agriculturally acceptable adjuvants include, but are not limited to, crop oil concentrate (mineral oil (85%) +emulsifiers (15%)), 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> alkylpolyglycoside, phosphate 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, emulsified methylated seed oil, tridecyl alcohol (synthetic) ethoxylate (8 EO), tallow amine ethoxylate (15 EO), and PEG(400) dioleate-99.

In some embodiments, the additive is a safener that is an organic compound leading to better crop plant compatibility when applied with a herbicide. In some embodiments, the safener itself is herbicidally active. In some, the safener acts as an antidote or antagonist in the crop plants and can reduce or prevent damage to the crop plants. Exemplary safeners include, but are not limited to, AD-67 (MON 4660), benoxacor, benthocarb, brassinolide, cloquintocet (mexyl), cyometrinil, cyprosulfamide, daimuron, dichlormid, dicyclonon, dietholate, dimepiperate, disulfoton, fenchlorazole, fenchlorazole-ethyl, fenclorim,

flurazole, fluxofenim, furilazole, harpin proteins, isoxadifen-ethyl, jiecaowan, jiecaoxi, mefenpyr, mefenpyr-diethyl, mephenate, naphthalic anhydride, 2,2,5-trimethyl-3-(dichloroacetyl)-1,3-oxazolidine, 4-(dichloroacetyl)-1-oxa-4-azaspiro [4.5]decane, oxabetrinil, R29148, and *N*-phenyl-sulfonylbenzoic acid amides, as well as thereof agriculturally acceptable salts and, provided they have a carboxyl group, their agriculturally acceptable derivatives. In some embodiments, the safener can be cloquintocet or an ester or salt thereof, such as cloquintocet (mexyl). For example, cloquintocet can be used to antagonize harmful effects of the compositions on rice and cereals.

Exemplary surfactants (e.g., wetting agents, tackifiers, dispersants, emulsifiers) include, but are not limited to, the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, for example lignosulfonic acids, phenolsulfonic acids, naphthalenesulfonic acids, and dibutyl naphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl sulfates, lauryl ether sulfates and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, and also of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalene sulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl or tributylphenyl polyglycol ether, alkyl aryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors and proteins, denatured proteins, polysaccharides (e.g., methylcellulose), hydrophobically modified starches, polyvinyl alcohol, polycarboxylates, polyalkoxylates, polyvinyl amine, polyethyleneimine, polyvinylpyrrolidone and copolymers thereof.

Exemplary thickeners include, but are not limited to, polysaccharides, such as xanthan gum, and organic and inorganic sheet minerals, and mixtures thereof.

Exemplary antifoam agents include, but are not limited to, silicone emulsions, long-chain alcohols, fatty acids, salts of fatty acids, organofluorine compounds, and mixtures thereof.

Exemplary antimicrobial agents include, but are not limited to, bactericides based on dichlorophen and benzyl alcohol hemiformal, and isothiazolinone derivatives, such as alkylisothiazolinones and benzisothiazolinones, and mixtures thereof.

Exemplary antifreeze agents, include, but are not limited to ethylene glycol, propylene glycol, urea, glycerol, and mixtures thereof.

Exemplary colorants include, but are not limited to, the dyes known under the names Rhodamin B, pigment blue 15:4, pigment blue 15:3, pigment blue 15:2, pigment blue 15:1, pigment blue 80, pigment yellow 1, pigment yellow 13, pigment red 112, pigment red 48:2, pigment red 48:1, pigment red 57:1, pigment red 53:1, pigment orange 43, pigment orange 34, pigment orange 5, pigment green 36, pigment green 7, pigment white 6, pigment brown 25, basic violet 10, basic violet 49, acid red 51, acid red 52, acid red 14, acid blue 9, acid yellow 23, basic red 10, basic red 108, and mixtures thereof.

Exemplary adhesives include, but are not limited to, polyvinylpyrrolidone, polyvinyl acetate, polyvinyl alcohol, tylose, and mixtures thereof.

In some embodiments, the additive includes a carrier. In some embodiments, the additive includes a liquid or solid carrier. In some embodiments, the additive includes an organic or inorganic carrier. Exemplary liquid carriers 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, 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, liquid fertilizers and the like, and water as well as mixtures thereof. Exemplary solid carriers include, but are not limited to, silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, pyrophyllite clay, attapulgus clay, kieselguhr, calcium carbonate, bentonite clay, Fuller's earth, cottonseed hulls, wheat flour, soybean flour, pumice, wood flour, walnut shell flour, lignin, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders, and mixtures thereof.

In some embodiments, emulsions, pastes or oil dispersions, can be prepared by homogenizing (a) and (b) in water by means of wetting agent, tackifier, dispersant or

emulsifier. In some embodiments, concentrates suitable for dilution with water are prepared, comprising (a), (b), a wetting agent, a tackifier, and a dispersant or emulsifier.

In some embodiments, powders or materials for spreading and dusts can be prepared by mixing or concomitant grinding of (a) and (b) and optionally a safener with a solid carrier.

In some embodiments, granules (e.g. coated granules, impregnated granules and homogeneous granules) can be prepared by binding the (a) and (b) to solid carriers.

The formulations disclosed herein can comprise a synergistic, herbicidally effective amount of (a) and (b). In some embodiments, the concentrations of (a) and (b) in the formulations can be varied. In some embodiments, the formulations comprise from 1% to 95% (e.g., from 5% to 95%, from 10% to 80%, from 20% to 70%, from 30% to 50%) by total weight of (a) and (b). In some embodiments, (a) and (b), independently, can be employed in a purity of from 90% to 100% (e.g., from 95% to 100%) according to NMR spectrometry. In some embodiments, the concentrations of (a), (b), and additional pesticides in the formulations can be varied. In some embodiments, the formulations comprise from 1% to 95% (e.g., from 5% to 95%, from 10% to 80%, from 20% to 70%, from 30% to 50%) by total weight of (a), (b), and additional pesticides. In some embodiments, (a), (b), and additional pesticides, independently, can be employed in a purity of from 90% to 100% (e.g., from 95% to 100%) according to NMR spectrometry.

### **Methods of Application**

The compositions disclosed herein can be applied in any known technique for applying herbicides. Exemplary application techniques include, but are not limited to, spraying, atomizing, dusting, spreading, or direct application into water (in-water), glycerine, or diesel. The compositions can be applied directly (e.g., low volume foliar, high volume foliar, cut stump, basal, or soil concentration) or by broadcast applications. The method of application can vary depending on the intended purpose. In some embodiments, the method of application can be chosen to ensure the finest possible distribution of the compositions disclosed herein.

The compositions disclosed herein can be applied pre-emergence (before the emergence of undesirable vegetation) or post-emergence (i.e., during and/or after emergence of the undesirable vegetation). In some embodiments, the compositions disclosed herein are applied post-emergence when the undesirable vegetation starts with leaf development up to flowering. In some embodiments, the compositions disclosed herein

are applied post-emergence to relatively immature undesirable vegetation to achieve the maximum control of weeds. In some embodiments when the compositions are used in crops, the compositions can be applied after seeding and before or after the emergence of the crop plants. In some embodiments, the compositions disclosed herein show good crop tolerance even when the crop has already emerged, and can be applied during or after the emergence of the crop plants. In some embodiments, when the compositions are used in crops, the compositions can be applied before seeding of the crop plants. In some embodiments, the compositions are used in mature trees or shrubs.

In some embodiments, the compositions disclosed herein are applied to vegetation or an area adjacent the vegetation or applying to soil or water to prevent the emergence or growth of vegetation by spraying (e.g., foliar spraying). For example, the composition can be applied aerially. In some embodiments, the spraying techniques use, for example, water as carrier and spray liquor rates of from 10 liters per hectare (L/ha) to 2000 L/ha (e.g., from 50 L/ha to 1000 L/ha, or from 100 to 500 l/ha). In some embodiments, the compositions disclosed herein are applied by the low-volume or the ultra-low-volume method, wherein the application is in the form of micro granules. In some embodiments, wherein the compositions disclosed herein are less well tolerated by certain crop plants, the compositions can be applied with the aid of the spray apparatus in such a way that they come into little contact, if any, with the leaves of the sensitive crop plants while reaching the leaves of undesirable vegetation that grows underneath or the bare soil (e.g., post-directed or lay-by).

In some embodiments, wherein the undesirable vegetation is treated post-emergence, the compositions disclosed herein are applied by foliar application. In some embodiments, herbicidal activity is exhibited by the compounds of the synergistic mixture when they are applied directly to the plant or to the locus of the plant at any stage of growth or before planting or emergence. The effect observed can depend upon the type of undesirable vegetation to be controlled, the stage of growth of the undesirable vegetation, the application parameters of dilution and spray drop size, the particle size of solid components, the environmental conditions at the time of use, the specific compound employed, the specific adjuvants and carriers employed, the soil type, and the like, as well as the amount of chemical applied. In some embodiments, these and other factors can be adjusted to promote non-selective or selective herbicidal action.

The compositions and methods disclosed herein can be used to control undesired vegetation in a variety of crop and non-crop applications. In some embodiments, the

compositions and methods disclosed herein can be used for controlling undesired vegetation in crops. In some embodiments, the compositions and methods disclosed herein can be used for controlling undesired vegetation in non-crop areas. Exemplary non-crop areas include, but are not limited to, turf, pasture, fallow, wildlife management areas, or rangeland. In some embodiments, the compositions and methods disclosed herein can be used in industrial vegetation management (IVM) or for utility, pipeline, roadside, and railroad rights-of-way applications. In some embodiments, the compositions and methods disclosed herein can also be used in forestry (e.g., for site preparation or for combating undesirable vegetation in plantation forests). In some embodiments, the compositions and methods disclosed herein can be used to control undesirable vegetation in conservation reserve program lands (CRP), trees, vines, grasslands, and grasses grown for seeds. In some embodiments, the compositions and methods disclosed herein can be used on lawns (e.g., residential, industrial, and institutional), golf courses, parks, cemeteries, athletic fields, and sod farms.

The compositions and methods disclosed herein can also be used in crop plants that are resistant to, for instance, herbicides, pathogens, and/or insects. The combination of (a), (b), and a complementary herbicide or salt or ester thereof can be used in combination with herbicides that are selective for the crop being treated and which complement the spectrum of weeds controlled by these compounds at the application rate employed.

The herbicidal compositions prepared disclosed herein are effective against a variety of types of undesirable vegetation. In some embodiments, the compositions disclosed herein can be used for controlling broadleaf weeds. Exemplary broadleaf weeds include, but are not limited to, *Polygonum* species such as wild buckwheat (*Polygonum convolvulus*), *Amaranthus* species such as pigweed (*Amaranthus retroflexus*), *Chenopodium* species such as common lambsquarters (*Chenopodium album* L.), *Sida* species such as prickly sida (*Sida spinosa* L.), *Ambrosia* species such as common ragweed (*Ambrosia artemisiifolia*), *Acanthospermum* species, *Anthemis* species, *Atriplex* species, *Cirsium* species, *Convolvulus* species, *Conyza* species, such as horseweed (*Conyza canadensis*), *Cassia* species, *Commelina* species, *Datura* species, *Euphorbia* species, *Geranium* species, *Galinsoga* species, morning-glory (*Ipomoea* species), *Lamium* species, *Malva* species, *Matricaria* species, *Prosopis* species, *Rumex* species, *Sysimbrium* species, *Solanum* species, *Trifolium* species, *Xanthium* species, *Veronica* species, *Viola* species, common chickweed (*Stella ria media*), velvetleaf (*Abutilon theophrasti*), Hemp sesbania (*Sesbania exaltata* Cory), *Anoda cristata*, *Bidens pilosa*, *Brassica kaber*, *Capsella bursa-pastoris*, *Centaurea cyanus*,

*Galeopsis tetrahit*, *Galium aparine*, *Helianthus annuus*, *Desmodium tortuosum*, *Kochia scoparia*, *Medicago arabica*, *Mercurialis annua*, *Myosotis arvensis*, *Papaver rhoeas*, *Raphanus raphanistrum*, *Salsola kali*, *Sinapis arvensis*, *Sonchus arvensis*, *Thlaspi arvense*, *Tagetes minuta*, *Richardia brasiliensis*, *Plantago major*, and *Plantago lanceolata*. In some embodiments, the undesirable vegetation includes honey mesquite (weed bayer: PRCJG).

By way of non-limiting illustration, examples of certain embodiments of the present disclosure are given below.

### Examples

#### Evaluation of Aminopyralid Triisopropanolamine Salt and Clopyralid Monoethanolamine Salt for Post-Emergence Synergistic Weed Control

Field trials were conducted with applications made to established grassland with naturally occurring weed populations. The target plants were treated with postemergence foliar applications when they reached two to five feet tall. All treatments were applied using a nonrandomized trial design, with three replications per treatment.

Treatments consisted of aminopyralid potassium salt and clopyralid-olamine, each in water and applied alone or in combination. Spray solutions were prepared using an appropriate amount of dilution to form a 2L aqueous spray solution with active ingredients in single and two way combinations. Formulated compounds were applied to the plant material with a backpack sprayer equipped with 8003 nozzles calibrated to deliver 187 L/ha at a spray height of about 18 inches (43 centimeters (cm)) above average plant canopy. The treated plants were honey mesquite (*Prosopis glandulosa*). The treated plots and control plots were rated blind at various intervals after application. Ratings were based on a scale of 0–100%, wherein 0% indicates no damage to the canopy of the undesired vegetation and 100% indicates complete destruction of the canopy of undesired vegetation. Dead and live plants were counted and the mortality was calculated as a % of the total number of undesired plants per plot.

Colby's equation was used to determine the herbicidal effects expected from the mixtures, as described above. The results were measured at 81, 82, 385, and 386 days after the first application of the compositions. The trials exhibited unexpected synergy, and those results were found statistically significant under the p-value test. The herbicide tank mix combinations tested, application rates and ratios employed, plant species tested, and results are given below.

|               |                     |                                                         | Aminopyralid<br>TIPA Salt 280<br>gae/ha | Clopyralid<br>MEA Salt<br>560 gae/ha | Combination                             |                                             |
|---------------|---------------------|---------------------------------------------------------|-----------------------------------------|--------------------------------------|-----------------------------------------|---------------------------------------------|
| Weed<br>Bayer | Evaluation          | Evaluation<br>Interval<br>( Days<br>after<br>Treatment) | Mean % weed<br>mortality                | Mean % weed<br>mortality             | Measured<br>mean %<br>weed<br>mortality | Colby predicted<br>mean % weed<br>mortality |
| PRCJG         | % Canopy<br>Control | 81                                                      | 22.0                                    | 370                                  | 75.0                                    | 49.3                                        |
| PRCJG         | % Canopy<br>Control | 82                                                      | 10.0                                    | 25.0                                 | 80.0                                    | 32.5                                        |
| PRCJG         | %Mortality          | 385                                                     | 0                                       | 25                                   | 63.2                                    | 25.0                                        |
| PRCJG         | %Mortality          | 386                                                     | 14                                      | 7                                    | 63.2                                    | 20.0                                        |

As shown above, the samples demonstrated synergistic weed control, with higher measured weed control than would be predicted by the Colby equation.

The compositions and methods of the appended claims are not limited in scope by the specific compositions and methods described herein, which are intended as illustrations of a few aspects of the claims and any compositions and methods that are functionally equivalent are intended to fall within the scope of the claims. Various modifications of the compositions and methods in addition to those shown and described herein are intended to fall within the scope of the appended claims. Further, while only certain representative compositions and method steps disclosed herein are specifically described, other combinations of the compositions and method steps also are intended to fall within the scope of the appended claims, even if not specifically recited. Thus, a combination of steps, elements, components, or constituents may be explicitly mentioned herein; however, other combinations of steps, elements, components, and constituents are included, even though not explicitly stated. The term “comprising” and variations thereof as used herein is used synonymously with the term “including” and variations thereof and are open, non-limiting terms. Although the terms “comprising” and “including” have been used herein to describe various embodiments, the terms “consisting essentially of” and “consisting of” can be used in place of “comprising” and “including” to provide for more specific embodiments of the invention and are also disclosed. Other than in the examples, or where otherwise noted, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood at the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, to be construed in light of the number of significant digits and ordinary rounding approaches.

**WHAT IS CLAIMED IS:**

1. A herbicidal composition comprising a synergistically herbicidal effective amount of (a) aminopyralid, or an agriculturally acceptable salt or ester thereof and (b) clopyralid, or an agriculturally acceptable salt or ester thereof.
2. The composition of claim 1, wherein (a) includes aminopyralid triisopropanolamine salt.
3. The composition of claim 1 or 2, wherein (b) includes clopyralid monoethanolamine salt.
4. The composition of any one of claims 1-3, wherein the acid equivalent weight ratio of (a) to (b) is from 1:373 to 24:1.
5. The composition of any one of claims 1-4, wherein the acid equivalent weight ratio of (a) to (b) is from 1:5 to 2:1.
6. The composition of any one of claims 1-5, further comprising an additional pesticide.
7. The composition of claim 6, wherein the additional pesticide includes one or more pesticides selected from the group consisting of aminocyclopyrachlor, amicarbazone, bromoxynil, chlorsulfuron, 2,4-D, dicamba, dichlorprop-P, diclosulam, diuron, florasulam, flucarbazone-sodium, flumetsulam, fluroxypyr, glyphosate, glufosinate, imazamox, imazapyr, imazapic, imazaquin, imazethapyr, imazamethabenz, indaziflam, ioxynil, MCPA, mecoprop-P, metsulfuron-methyl, oxyfluorfen, penoxsulam, picloram, pinoxaden, pyroxsulam, rimsulfuron, thifensulfuron-methyl, tebuthiuron, tribenuron-methyl, triclopyr, and agriculturally acceptable salts or esters or mixtures thereof.
8. The composition of claim 7, wherein the additional pesticide includes 2,4-D choline salt, triclopyr choline salt, aminocyclopyrachlor choline salt, or a mixture thereof.
9. The composition of any one of claims 1-8, further comprising a herbicidal safener.
10. The composition of any one of claims 1-9, further comprising an agriculturally acceptable adjuvant or carrier.
11. The composition of any one of claims 1-10, which is synergistic as determined by the Colby equation.

12. The composition of any one of claim 1-11, wherein the composition is provided as a herbicidal concentrate.
13. A method of controlling undesired vegetation, which comprises applying to the undesired vegetation or an area adjacent the undesired vegetation or applying to soil or water to prevent the emergence or growth of the undesired vegetation (a) aminopyralid, or an agriculturally acceptable salt or ester thereof and (b) clopyralid, or an agriculturally acceptable salt or ester thereof,  
wherein (a) and (b) are each added in an amount sufficient to produce a synergistic herbicidal effect.
14. The method of claim 13, wherein (a) and (b) are applied postemergence.
15. The method of claim 13 or 14, wherein the undesired vegetation is honey mesquite.
16. The method of any one of claims 13-15, wherein the undesirable vegetation is controlled in CRP, fallow land, range and pasture, IVM, or tree and vine.
17. A method of controlling honey mesquite in CRP, fallow land, range and pasture, IVM, or tree and vine, which comprises applying postemergence to the honey mesquite or an area adjacent the honey mesquite (a) aminopyralid, or an agriculturally acceptable salt or ester thereof and (b) clopyralid, or an agriculturally acceptable salt or ester thereof,  
wherein (a) and (b) are each added in an amount sufficient to produce a synergistic herbicidal effect.
18. The method of any one of claims 13-17, wherein (a) and (b) are applied simultaneously.
19. The method of any one of claims 13-18, wherein (a) includes aminopyralid triisopropanolamine salt.
20. The method of any one of claims 13-19, wherein (b) includes clopyralid monoethanolamine salt.
21. The method of any one of claims 13-20, wherein (a) and (b) are applied in an acid equivalent weight ratio of (a) to (b) from 1:373 to 24:1.
22. The method of any one of claims 13-21, wherein (a) and (b) are applied in an acid equivalent weight ratio of (a) to (b) from 1:5 to 2:1.

23. The method of any one of claims 13-22, further comprising applying an additional pesticide.

24. The method of claim 23, wherein the additional pesticide includes one or more pesticides selected from the group consisting of aminocyclopyrachlor, amicarbazone, bromoxynil, chlorsulfuron, 2,4-D, dicamba, dichlorprop-P, diclosulam, diuron, florasulam, flucarbazone-sodium, flumetsulam, fluroxypyr, glyphosate, glufosinate, imazamox, imazapyr, imazapic, imazaquin, imazethapyr, imazamethabenz, indaziflam, ioxynil, MCPA, mecoprop-P, metsulfuron-methyl, oxyfluorfen, penoxsulam, picloram, pinoxaden, pyroxsulam, rimsulfuron, thifensulfuron-methyl, tebuthiuron, tribenuron-methyl, triclopyr, and agriculturally acceptable salts or esters or mixtures thereof.

25. The method of claim 24, wherein the additional pesticide includes 2,4-D choline salt, triclopyr choline salt, aminocyclopyrachlor choline salt, or a mixture thereof.

26. The method of any one of claims 13-25, further comprising applying a herbicidal safener.

27. The method of any one of claims 13-26, further comprising applying an agriculturally acceptable adjuvant or carrier.

28. The method of any one of claims 13-27, wherein (a) and (b) are synergistic as determined by the Colby equation.

29. The method of any one of claims 13-28, wherein (a) is applied in an amount of from 3–480 g ae/ha.

30. The method of any one of claims 13-29, wherein (b) is applied in an amount of from 20–1120 g ae/ha.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/69797

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A01N 43/34 (2013.01)

USPC - 504/155

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)

IPC(8) - A01N 43/34 (2013.01)

USPC - 504/155

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

USPC - 504/155, 167, 176

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Google Patents, Google Scholar, WIPO (Honey, mesquite, synergistic, monoethanolamine, aminopyralid, clopyralid, trisopropanolamine, tri-isopropanol, monoethanol, mono-ethanol, postemergenc, herb, veg, weed, synergistic)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category*     | Citation of document, with indication, where appropriate, of the relevant passages                                                        | Relevant to claim No.            |
|---------------|-------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|
| X<br>---<br>Y | US 2008/0242546 A1 (SCHULTZ, et al.) 02 October 2008 (02.10.2008) entire document, especially para [0007]-[0009], [0011], [0018]; claim 8 | 1, 13-14<br>-----<br>2-3, 15, 17 |
| Y             | US 2012/0142532 A1 (WRIGHT, et al.) 07 June 2012 (07.06.2012) entire document, especially para [0003], [0025]                             | 2-3                              |
| Y             | US 2011/0136667 A1 (TURNER, et al.) 09 June 2011 (09.06.2011) entire document, especially para [0004], [0152], [0160]                     | 15, 17                           |

☐ Further documents are listed in the continuation of Box C.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

31 January 2013 (31.01.2013)

Date of mailing of the international search report

28 FEB 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents  
P.O. Box 1450, Alexandria, Virginia 22313-1450

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PCT OSP: 571-272-7774

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/69797

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

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

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☒ Claims Nos.: 4-12, 16, 18-30  
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:

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.