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(54) Title: CLOQUINTOCET SALTS FOR SAFENING PYROXSULAM COMPOSITIONS

(57) Abstract: Disclosed herein is a herbicidal composition comprising a herbicidally effective amount of (a) pyroxsulam or an agriculturally acceptable salt thereof and (b) a cloquintocet salt. Also disclosed herein are methods of controlling undesirable vegetation with the compositions disclosed herein without excessive injury to desirable crops.

CLOQUINTOCET SALTS FOR SAFENING PYROXSULAM COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 62/280,281, filed January 19, 2016, which is hereby incorporated herein by reference in its entirety.

BACKGROUND

Controlling the growth of undesirable vegetation that can negatively affect the growth of desirable vegetation such as crops is a recurring issue in agriculture. A variety of herbicides and herbicidal formulations effective in controlling such unwanted growth have been developed.

In some cases, although a herbicide may be effective in controlling undesirable vegetation, it may also have a phytotoxic effect on a crop and cause injury or even kill the crop. Cloquintocet (CQC) is a quinoline compound that functions as a herbicidal safener by reducing the phytotoxic effects of the herbicide on crops to which it is applied. Cloquintocet has traditionally been provided as the 1-methylhexyl ester, i.e., cloquintocet-mexyl (CQC-M), which is also known as the 2-heptyl ester.

Although CQC-M is an effective safener, it has certain properties that make it difficult to handle and use in some situations, such as (1) an incompatibility with water leading to crystal formation, clogging of spray nozzles and/or loss of its safening properties, (2) a potential for ester hydrolysis in aqueous formulations, and (3) a low melting point making processing and storage of granular formulations challenging. Therefore, there is a desire in the art to provide effective safeners for crops that have improved compatibility with water.

SUMMARY

Herbicidal compositions containing a herbicidally effective amount of: (a) pyroxsulam or an agriculturally acceptable salt thereof, and (b) a cloquintocet salt are described herein. In some embodiments, the weight ratio of (a) in grams active ingredient (g ai) to (b) in grams acid equivalent (g ae) in the described compositions is from about 1:4 to about 1:0.5. In some embodiments, (a) is applied in an amount of from 4-40 g ai/ha. In some embodiments, (b) is applied in an amount of from 10-80 g ae/ha.

In some embodiments the cloquintocet salt contains a cation of the formula $N(R^1)(R^2)(R^3)(R^4)^+$, wherein R^1, R^2, R^3, and R^4 are independently H, C_1-C_4 alkyl, or C_1-C_4

hydroxyalkyl. In some embodiments, the cloquintocet salt is a primary ammonium salt, such as monoethanolammonium, monoisopropanolammonium, and isopropylammonium; a secondary ammonium salt, such as diethanolammonium, diisopropanolammonium, diethylammonium, dimethylammonium; a tertiary ammonium salt, such as, triethanolammonium, triisopropanolammonium, N,N-dimethylethanolammonium; a quaternary ammonium salt, such as choline; or mixtures thereof.

In some embodiments, the composition is a liquid composition selected from an aqueous suspension concentrate (SC), or an aqueous suspension emulsion (i.e., a suspoemulsion or an SE) concentrate, or a solid composition selected from a water-soluble granule (SG) or a water-dispersible granule (DG). In some embodiments, the composition is an aqueous spray solution or mixture. In some embodiments, the composition can further include an additional pesticide. In some embodiments, the additional pesticide can be a herbicide.

In some embodiments the compositions described herein that are SC or SE compositions may contain, with respect to the total composition, from about 5 grams active ingredient per liter (gai/L) to about 150 gai/L of pyroxsulam, or an agriculturally acceptable salt thereof, and from about 10 grams acid equivalent per liter (gae/L) to about 250 gae/L of a salt of cloquintocet.

In some embodiments the compositions described herein that are SG or DG compositions may comprise, with respect to the total composition, from about 5 grams active ingredient per kilogram (gai/kg) to about 150 gai/kg of pyroxsulam, or an agriculturally acceptable salt thereof, and from about 10 grams acid equivalent per kilogram (gae/kg) to about 250 gae/kg of a salt of cloquintocet.

In some embodiments, the compositions described herein may offer improved safety to those handling such compositions should the compositions accidentally be splashed onto or otherwise injected into their eyes. In some embodiments, an aqueous solution containing one or more of certain cloquintocet salts exhibit a lower potential for eye irritancy than an aqueous solution containing other forms of cloquintocet.

Also disclosed herein are methods of controlling undesirable vegetation which comprises contacting the vegetation or the locus thereof with or applying to the soil or water to prevent the emergence or growth of vegetation any of the compositions disclosed herein. In some embodiments, the composition is applied postemergence to the undesirable vegetation. In some embodiments, the undesirable vegetation is controlled in crops such as wheat, barley, triticale, teff, oats, sorghum, corn, rice, sugarcane, or pasture grasses without significant adverse effects to

the crops. In some embodiments, the undesirable vegetation is selected from the group consisting of wild oat, annual ryegrass, and combinations thereof.

DETAILED DESCRIPTION

Described herein are herbicidal compositions containing a herbicidally effective amount of (a) pyroxsulam or an agriculturally acceptable salt thereof and (b) a cloquintocet salt, wherein the cloquintocet salt contains a cation of the formula $N(R^1)(R^2)(R^3)(R^4)^+$, wherein R^1, R^2, R^3, and R^4 are independently H, C_1-C_4 alkyl, or C_1-C_4 hydroxyalkyl.

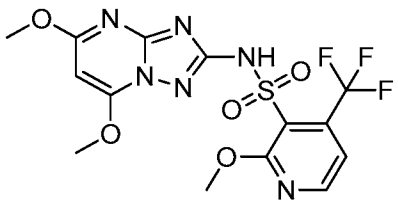
I. Definitions

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 "crops" and "vegetation" can include, for instance, germinant seeds, emerging seedlings, and established vegetation.

The term "pesticide," as used herein, means a herbicide, an insecticide, or a fungicide.

II. Pyroxsulam

Compositions and methods described herein can include pyroxsulam (*i.e.*, N-(5,7-dimethoxy[1,2,4]triazolo[1,5-a]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)pyridine-3-sulfonamide) or an agriculturally acceptable salt thereof. Pyroxsulam is a triazolopyrimidine sulfonamide herbicide that provides broad-spectrum control of many annual, biannual, and perennial weeds, and has the following structure.



As a member of the triazolopyrimidine sulfonamide class of chemistry, pyroxsulam inhibits the plant enzyme acetolactate synthase (ALS), which is essential for the synthesis of branched-chain amino acids valine, leucine, and isoleucine. Inhibition of amino acid production subsequently inhibits cell division and causes death in susceptible plants.

Pyroxsulam is a systemic, phloem and xylem mobile herbicide that is absorbed via leaves, shoots and roots. The leaves and roots are the primary uptake sites in plants. The compound is translocated to meristematic tissue. Visible symptoms include stunting and chlorosis, followed by necrosis and then death.

Pyroxsulam is or has been commercially available, for example, from Dow AgroSciences, LLC under the trademarks ADMITT®, CRUSADER®, QUASAR®, MERIT®, POWERFLEX®, SIMPLICITY®, ACROSS®, and BROADWAY®. Its herbicidal activity is described in The Pesticide Manual, Fifteenth Edition, 2009.

In some embodiments, the compositions described herein that are liquid compositions (i.e., SC and SE) can comprise, with respect to the total composition, from about 5 grams active ingredient per liter (gai/L) to about 100 gai/L of pyroxsulam, from about 5 gai/L to about 90 gai/L of pyroxsulam, from about 5 gai/L to about 80 gai/L of pyroxsulam, from about 5 gai/L to about 70 gai/L of pyroxsulam, from about 5 gai/L to about 60 gai/L of pyroxsulam, from about 5 gai/L to about 50 gai/L of pyroxsulam, from about 5 gai/L to about 40 gai/L of pyroxsulam, from about 5 gai/L to about 30 gai/L of pyroxsulam, from about 5 gai/L to about 20 gai/L of pyroxsulam, or from about 5 gai/L to about 15 gai/L of pyroxsulam, or an agriculturally acceptable salt thereof. In some embodiments the liquid, aqueous compositions described herein may comprise from about 10 gai/L to about 100 gai/L of pyroxsulam, from about 20 gai/L to about 100 gai/L of pyroxsulam, from about 30 gai/L to about 100 gai/L of pyroxsulam, from about 40 gai/L to about 100 gai/L of pyroxsulam, from about 50 gai/L to about 100 gai/L of pyroxsulam, from about 60 gai/L to about 100 gai/L of pyroxsulam, from about 70 gai/L to about 100 gai/L of pyroxsulam, from about 80 gai/L to about 100 gai/L of pyroxsulam, or from about 90 gai/L to about 100 gai/L of pyroxsulam, or an agriculturally acceptable salt thereof. In some embodiments the liquid, aqueous compositions described herein may comprise from about 10 gai/L to about 50 gai/L of pyroxsulam, from about 20 gai/L to about 40 gai/L of pyroxsulam, from about 25 gai/L to about 35 gai/L of pyroxsulam, from about 50 gai/L to about 90 gai/L of pyroxsulam, from about 60 gai/L to about 80 gai/L of pyroxsulam, or from about 70 gai/L to about 80 gai/L of pyroxsulam, or an agriculturally acceptable salt thereof.

In some embodiments the compositions described herein that are solid compositions, such as SG and DG compositions, which can comprise, with respect to the total composition, from about 1 grams active ingredient per liter (gai/kg) to about 500 gai/kg of pyroxsulam, or an agriculturally acceptable salt thereof, or from about 5 gai/kg to about 500 gai/kg, from about 10

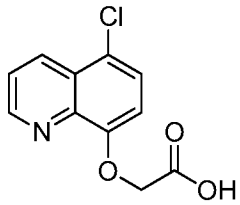
gai/kg to about 400 gai/kg, from about 10 gai/kg to about 300 gai/kg, from about 20 gai/kg to about 300 gai/kg, from about 50 gai/kg to about 300 gai/kg, from about 50 gai/kg to about 250 gai/kg, from about 50 gai/kg to about 200 gai/kg, or from about 50 gai/kg to about 150 gai/kg of pyroxsulam, or an agriculturally acceptable salt thereof.

In some embodiments the liquid, aqueous compositions described herein that are aqueous spray mixtures or solutions may comprise from about 0.001 to about 2.0 wt% of pyroxsulam, from about 0.01 to about 1.0 wt% of pyroxsulam, from about 0.01 to about 0.5 wt% of pyroxsulam, or from about 0.01 to about 0.1 wt% of pyroxsulam.

Pyroxsulam is particularly problematic with respect to injury to commercially valuable grass crops, such as wheat (e.g., Spring wheat, Durum wheat), oats (e.g., Wild Oats), barley and sorghum and broadleaf crops, such as field pea, clovers, turnip, and other brassica species. As the data shows, the use of CQC salts shows significantly less injury compared to the mexyl ester of CQC (CQC-M). This is unexpected since it has generally been shown that CQC-M is taken up better by the crops than the free acid due to its increased lipophilicity.

III. Cloquintocet salts

Cloquintocet (CQC) is a quinoline compound that has the following chemical structure.



Cloquintocet is a safener that is normally used as the mexyl ester, is applied in combination with herbicides, and is useful for reducing phytotoxicity to crops such as wheat, barley, triticale, rye, teff, oats, corn, sorghum, rice, sugar cane, and pasture grasses. Herbicide safeners are molecules used in combination with herbicides to make them "safer" – that is, to reduce the effect of the herbicide on crop plants, and to improve selectivity between crop plants vs. weed species being targeted by the herbicide. Herbicide safeners can be used to pre-treat crop seeds prior to planting, or they can be sprayed on plants as a mixture with the herbicide.

The cloquintocet is provided herein as a cloquintocet salt comprising a cation of the formula $N(R^1)(R^2)(R^3)(R^4)^+$, wherein R^1, R^2, R^3, and R^4 are independently H, C_1-C_4 alkyl, or C_1-C_4 hydroxyalkyl. In some embodiments, the cloquintocet salt is a primary ammonium salt, such

as monoethanolammonium, monoisopropanolammonium, and isopropylammonium; a secondary ammonium salt, such as diethanolammonium, diisopropanolammonium, diethylammonium, dimethylammonium; a tertiary ammonium salt, such as triethanolammonium, triisopropanolammonium, N,N-dimethylethanolammonium; a quaternary ammonium salt, such as choline; or mixtures thereof. In some embodiments, the cloquintocet salt includes cloquintocet choline salt (CQC-choline).

In some embodiments, the compositions described herein that are liquid, compositions (i.e., SC and SE compositions) may contain, with respect to the total composition, from about 10 grams acid equivalent per liter (gae/L) to about 250 gae/L of a salt of cloquintocet, from about 20 gae/L to about 225 gae/L of a salt of cloquintocet, from about 20 gae/L to about 200 gae/L of a salt of cloquintocet, from about 30 gae/L to about 200 gae/L of a salt of cloquintocet, from about 40 gae/L to about 200 gae/L of a salt of cloquintocet, from about 50 gae/L to about 200 gae/L of a salt of cloquintocet, from about 60 gae/L to about 200 gae/L of a salt of cloquintocet, from about 70 gae/L to about 200 gae/L of a salt of cloquintocet, from about 80 gae/L to about 200 gae/L of a salt of cloquintocet, from about 90 gae/L to about 200 gae/L of a salt of cloquintocet, from about 100 gae/L to about 200 gae/L of a salt of cloquintocet, from about 120 gae/L to about 200 gae/L of a salt of cloquintocet, from about 140 gae/L to about 200 gae/L of a salt of cloquintocet, from about 160 gae/L to about 200 gae/L of a salt of cloquintocet, or from about 180 gae/L to about 200 gae/L of a salt of cloquintocet. In some embodiments the liquid, aqueous compositions described herein may comprise from about 10 gae/L to about 180 gae/L of a salt of cloquintocet, from about 10 gae/L to about 160 gae/L of a salt of cloquintocet, from about 10 gae/L to about 160 gae/L of a salt of cloquintocet, from about 10 gae/L to about 140 gae/L of a salt of cloquintocet, from about 10 gae/L to about 120 gae/L of a salt of cloquintocet, from about 10 gae/L to about 100 gae/L of a salt of cloquintocet, from about 10 gae/L to about 90 gae/L of a salt of cloquintocet, from about 10 gae/L to about 80 gae/L of a salt of cloquintocet, from about 10 gae/L to about 70 gae/L of a salt of cloquintocet, from about 10 gae/L to about 60 gae/L of a salt of cloquintocet, from about 10 gae/L to about 50 gae/L of a salt of cloquintocet, from about 10 gae/L to about 40 gae/L of a salt of cloquintocet, from about 10 gae/L to about 30 gae/L of a salt of cloquintocet, or from about 20 gae/L to about 30 gae/L of a salt of cloquintocet. In some embodiments the liquid, aqueous compositions described herein may comprise from about 20 gae/L to about 100 gae/L of a salt of cloquintocet, from about 30 gae/L to about 90 gae/L of a salt of cloquintocet, from about 40 gae/L to about 80 gae/L of a salt

of cloquintocet, from about 50 gae/L to about 70 gae/L of a salt of cloquintocet, from about 60 gae/L to about 70 gae/L of a salt of cloquintocet, from about 60 gae/L to about 150 gae/L of a salt of cloquintocet, from about 70 gae/L to about 140 gae/L of a salt of cloquintocet, from about 80 gae/L to about 130 gae/L of a salt of cloquintocet, from about 90 gae/L to about 120 gae/L of a salt of cloquintocet, or from about 100 gae/L to about 110 gae/L of a salt of cloquintocet.

In some embodiments the compositions described herein that are solid compositions (i.e., SG and DG) may contain, with respect to the total composition, from about 10 grams acid equivalent per kilogram (gae/kg) to about 250 gae/kg of a salt of cloquintocet, from about 20 gae/kg to about 225 gae/kg of a salt of cloquintocet, from about 20 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 30 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 40 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 50 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 60 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 70 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 80 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 90 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 100 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 120 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 140 gae/kg to about 200 gae/kg of a salt of cloquintocet, from about 160 gae/kg to about 200 gae/kg of a salt of cloquintocet, or from about 180 gae/kg to about 200 gae/kg of a salt of cloquintocet. In some embodiments the solid compositions described herein may comprise from about 10 gae/kg to about 180 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 160 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 160 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 140 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 120 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 100 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 90 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 80 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 70 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 60 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 50 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 40 gae/kg of a salt of cloquintocet, from about 10 gae/kg to about 30 gae/kg of a salt of cloquintocet, or from about 20 gae/kg to about 30 gae/kg of a salt of cloquintocet. In some embodiments the solid compositions described herein may comprise from about 20 gae/kg to about 100 gae/kg of a salt of cloquintocet, from about 30 gae/kg to about 90 gae/kg of a salt of cloquintocet, from about 40 gae/kg to about 80 gae/kg of a salt of cloquintocet, from about 50 gae/kg to about 70 gae/kg of a

salt of cloquintocet, from about 60 gae/kg to about 70 gae/kg of a salt of cloquintocet, from about 60 gae/kg to about 150 gae/kg of a salt of cloquintocet, from about 70 gae/kg to about 140 gae/kg of a salt of cloquintocet, from about 80 gae/kg to about 130 gae/kg of a salt of cloquintocet, from about 90 gae/kg to about 120 gae/kg of a salt of cloquintocet, or from about 100 gae/kg to about 110 gae/kg of a salt of cloquintocet.

In some embodiments the compositions described herein that are aqueous spray solutions or mixtures may contain, with respect to the total composition, from about 0.005 to about 2.0 wt% ae of a salt of cloquintocet, from about 0.05 to about 1.0 wt% of a salt of cloquintocet, from about 0.05 to about 0.5 wt% of a salt of cloquintocet, or from about 0.05 to about 0.2 wt% of a salt of cloquintocet.

In some embodiments, an aqueous solution containing one or more of certain cloquintocet salts exhibit a lower potential for eye irritancy than an aqueous solution containing the free acid form of cloquintocet or the ammonium salt form of cloquintocet. In some examples, the cloquintocet salt exhibits a neutral red release assay NRR50 value of at least 15 mg ae/mL. For example, the cloquintocet salt can exhibit an NRR50 value of at least 20, at least 35, at least 50, at least 70, at least 90, at least 120, at least 150, at least 180, or at least 210 mg ae/mL.

IV. Herbicidal mixtures or combinations

The (a) pyroxsulam or an agriculturally acceptable salt thereof, is mixed with or applied in combination with (b) a cloquintocet salt as described herein. In some embodiments, the weight ratio of (a) to (b) is from 1:4 to 1:0.5. In some embodiments, the weight ratio of (a) to (b), can be at least 1:4, for example at least 1:3.75, 1: 3.5, 1:3.25, 1:3, 1:2.75, 1:2.5, 1:2.25, 1:2, 1:1.75, 1:1.5, 1:1.25, 1:1, or 1:0.75. In some embodiments, the weight ratio of (a) to (b) can be 1:0.5 or less, for example 1:0.7 or less, 1:0.9 or less, 1:1 or less, 1:1.25 or less, 1:1.5 or less, 1:1.75 or less, 1:2 or less, 1:2.25 or less, 1:2.5 or less, 1:2.75 or less, 1:3 or less, 1:3.25 or less, 1:3.5 or less, 1:3.75 or less. In some embodiments, the weight ratio of (a) to (b) can be from 1:4 to 1:0.5, from 1:3.75 to 1:0.75, from 1:3.5 to 1:1, from 1:3.4 to 1:1.25, from 1:3.3 to 1:1.5, from 1:3.2 to 1:1.75, or from 1:3 to 1:2.

V. Eye irritancy

Water soluble salts of certain carboxylic acids present in some aqueous agrochemical formulations can be irritating if accidentally splashed or otherwise injected into the eye of

anyone handling such a formulation. This property may lead to restrictive labeling of the products that limits their usefulness in certain markets, even where the active ingredient itself provides no such hazard.

The neutral red release (NRR) assay is an *in vitro* cytotoxicity test that can be used to measure the immediate toxic effects of test substances on cell membranes, resulting in the leaking of intracellular contents. The assay has already been used for several years to evaluate the cytotoxicities of various kinds of products, such as cosmetics, pharmaceuticals, industrial chemicals and household products. It has undergone in-house validation by many companies, and has been found to be particularly useful for identifying substances that are potentially capable of causing adverse reactions on coming into brief contact with the eye or the skin at relatively high concentrations, such as might occur in an adventitious splash into the eye or onto the skin, followed by a quick rinse. See the following literature for further information on this test: Reader, S. J., Blackwell, V., O'Hara, R, Clothier, R H., Griffin, G., and Balls, M., "A vital dye release method for assessing the short-term cytotoxic effects of chemicals and formulations," *ATLA,* 17, 28-37 (1989); Balls, M., Reader, S., Atkinson, K., Tarrant, J., and Clothier, R. H., "Non-animal alternative toxicity tests for detergents: Genuine replacements or mere prescreens?" *Chern. Tech. Biotechnol.* 50, 423-433 (1992); and Clothier, R. H., "The FRAME neutral red release assay," INVITTOX Protocol number 54 (1992).

In some examples, the pyroxsulam composition including the cloquintocet salt exhibits low levels of eye irritancy. In some examples, the pyroxsulam composition including the cloquintocet salt exhibits a lower potential for eye irritancy than the free acid form or ammonium salt form of cloquintocet. In some examples, the composition exhibits a neutral red release assay NRR50 value of at least 5 mg ae/mL of the cloquintocet salt. For example, the composition can exhibit an NRR50 value of at least 10, at least 20, at least 30, at least 40, at least 50, at least 60, at least 70, at least 80, at least 90, at least 100, or at least 110 mg ae/mL of the cloquintocet salt.

VI. 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) pyroxsulam, or an agriculturally acceptable salt thereof, and (b) a cloquintocet salt, wherein the cloquintocet salt contains a cation of the formula $N(R^1)(R^2)(R^3)(R^4)^+$, wherein R^1, R^2, R^3, and R^4 are independently H, C_1-C_4 alkyl, or C_1-C_4

hydroxyalkyl. 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, and/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, emulsions, microemulsions, suspoemulsions, oil dispersions, pastes, dusts, and materials for spreading or granules. In some examples, the formulation of (a) and (b) is an aqueous suspension concentrate. In some examples, the formulation of (a) and (b) is a suspension emulsion (i.e., a suspoemulsion) concentrate. In some examples, the formulation of (a) and (b) is a water-soluble granule or water-dispersible granule.

A. Additives

The compositions and methods disclosed herein can also include the use of an additive. In some embodiments, the additive can be diluted in water or can be in a more concentrated form. 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 pyroxsulam or an agriculturally acceptable salt thereof. In some embodiments, the additive is premixed with the cloquintocet salt. In some embodiments, the additive is premixed with the pyroxsulam or an agriculturally acceptable salt thereof, and the cloquintocet salt. In some embodiments the additive may be tank-mixed with the compositions described herein at the point of use. When the compositions described herein are used in combination with an additive that is an active ingredient, the presently claimed compositions can be formulated with the other

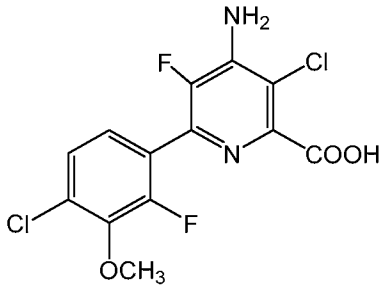
active ingredient or active ingredients as herbicidal solid or liquid compositions, tank mixed in water with the other active ingredient or active ingredients for simultaneous spray application, or applied sequentially with the other active ingredient or active ingredients in separate solid or spray applications.

1. Herbicides

In some embodiments, the additive is a pesticide. Exemplary pesticides that are herbicides include, but are not limited to, 2,4-D, acetochlor, aclonifen, ametryn, amicarbazone, 4-aminopicolinic acid based herbicides, such as halauxifen, halauxifen-methyl, and those described in U.S. Patent Nos. 7,314,849 and 7,432,227 to Balko, *et al.*, amidosulfuron, aminocyclopyrachlor, aminopyralid, aminotriazole, ammonium thiocyanate, anilofos, asulam, azimsulfuron, atrazine, beflubutamid, benazolin, benfuresate, bensulfuron-methyl, bentazone, bentazon-sodium, benzofenap, bifenox, bispyribac-sodium, bicyclopyrone, bromobutide, bromacil, bromoxynil, butachlor, butafenacil, butralin, butroxydim, carbetamide, cafenstrole, carfentrazone, carfentrazone-ethyl, chlormequat, clopyralid, chlorsulfuron, chlortoluron, cinidon-ethyl, clethodim, clodinafop-propargyl, clomeprop, clomazone, cloransulam-methyl, cyanazine, cyclosulfamuron, cycloxydim, cyhalofop , cyhalofop-butyl, daimuron, dicamba, dichlobenil, dichlorprop, dichlorprop-P, diclofop-methyl, diclosulam, diflufenican, diflufenzopyr, dimefuron, dimethachlor, diquat, diuron, s-ethyl dipropylcarbamothioate (EPTC), ET-751, esprocarb, ethoxysulfuron, etobenzanid, fenoxaprop, fenoxaprop-ethyl, fenoxaprop-ethyl+isoxidifen-ethyl, fenoxaprop-p-ethyl, fenoxasulfone, fentrazamide, flazasulfuron, florasulam, fluazifop, fluazifop-P-butyl, flucarbazone, flucabazone-sodium, flucetosulfuron (LGC-42153), flufenacet, flumetsulam, flumioxazin, flupyrsulfuron, flurochloridone, fluroxypyr, fluroxypyr-meptyl, flurtamone, gibberellic acid, glufosinate, glufosinate-ammonium, glyphosate, halosulfuron-methyl, haloxyfop-methyl, haloxyfop-R, haloxyfop-R-methyl, hexazinone, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, indanofan, indaziflam, iodosulfuron, iodosulfuron-ethyl-sodium, ioxynil, ipfencarbazone, isoproturon, isoxaben, isoxaflutole, lactofen, linuron, MCPA, MCPB, mecoprop , mecoprop-P, mefenacet, mesosulfuron, mesosulfuron-ethyl sodium, mesotrione, metamifop, metazochlor, metazosulfuron, metosulam, metribuzin, metsulfuron, metsulfuron-methyl, molinate, MSMA, 1-napthaleneacetic acid, napropamide, norfurazon, orthosulfamuron, oryzalin, oxadiargyl, oxadiazon, oxazichlomefone, oxyfluorfen, paraquat, pendimethalin, penoxsulam, pentoxazone, pethoxamid, picloram, picolinafen, pinoxaden, piperophos, pretilachlor, primisulfuron,

profluazol, profoxydim, prometon, propanil, propaquizafop, propyrisulfuron, propoxycarbazone, propyzamide, prosulfocarb, prosulfuron, pyraclonil, pyraflufen-ethyl, pyrasulfotole, pyroxasulfone, pyrazosulfuron, pyrazosulfuron-ethyl, pyrazolynate, pyribenzoxim (LGC-40863), pyributicarb, pyridate, pyriftalid, pyrimisulfan, pyroxsulam, pyroxasulfone, quinclorac, quinmerac, quizalofop-ethyl-D, quizalofop-P-ethyl, quizalofop-p-tefuryl, rimsulfuron, sethoxydim, simazine, sulfentrazone, sulfometuron, sulfosate, sulfosulfuron, tebuthiuron, tefuryltrione, tepraloxidim, terbacil, terbuthylazine, terbutryn, thenylchlor, thiazopyr, thiencarbazone-methyl, thifensulfuron, thifensulfuron-methyl, thiobencarb, topramezone, tralkoxydim, triafamone, triasulfuron, tribenuron, tribenuron-methyl, triafamone, triclopyr, and trifluralin, and agriculturally acceptable salts, choline salts, esters and mixtures thereof.

In some embodiments, the additive is a herbicide having the following formula



or a C_1-C_{12} alkyl or C_7-C_{12} arylalkyl ester or salt thereof, *e.g.*, the benzyl ester, referred to herein as Compound A.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, and a cloquintocet salt. In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and a herbicide selected from florasulam, penoxsulam, diclosulam, cloransulam-methyl, flumetsulam, metosulam, halauxifen-methyl, and Compound A. In some embodiments, the composition includes halauxifen-methyl and/or florasulam.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and a herbicide selected from mesosulfuron, metsulfuron, thifensulfuron, tribenuron, triasulfuron, thiencarbazone, flucarbazone, flupyrsulfuron, sulfosulfuron.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and a herbicide selected from imazamox, imazapyr, and imazethapyr.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and a herbicide selected from the group consisting of pinoxaden, clodinafop, fenoxyprop, and tralkoxydim.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and a herbicide selected from pyrasulfotole, topramezone, and bicylopyrone.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and clopyralid. In some embodiments, the clopyralid is a clopyralid salt. In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and aminopyralid.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and 2,4-D. In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and a herbicide selected from MCPA mad MCPB. In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and dicamba. In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and picloram. In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and triclopyr.

In some embodiments, the described compositions include pyroxsulam, fluroxypyr-meptyl, a cloquintocet salt, and a herbicide selected from tebuthiuron, isoxaben, thiazopyr, trifluralin and propyzamide.

In some embodiments, the described compositions include pyroxsulam, florasulam and a cloquintocet salt.

In some embodiments, the described compositions include pyroxsulam, a clopyralid salt and a cloquintocet salt.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl and a cloquintocet salt.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and a herbicide selected from florasulam, penoxsulam, diclosulam, cloransulam-methyl, flumetsulam, metosulam, and Compound A.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and a herbicide selected from mesosulfuron, metsulfuron,

thifensulfuron, tribenuron, triasulfuron, thiencarbazone, flucarbazone, flupyrsulfuron, and sulfosulfuron.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and a herbicide selected from imazamox, imazapyr, and imazethapyr.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and a herbicide selected from pinoxaden, clodinafop, fenoxyprop, and tralkoxydim.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and a herbicide selected from pyrasulfotole, topramezone, and bicylopyrone.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and clopyralid. In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and aminopyralid.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and 2,4-D. In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and a herbicide selected from MCPA and MCPB. In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and dicamba. In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and picloram. In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and triclopyr.

In some embodiments, the described compositions include pyroxsulam, halauxifen-methyl, a cloquintocet salt, and a herbicide selected from tebuthiuron, isoxaben, thiazopyr, trifluralin, and propyzamide.

In some embodiments, the described compositions include pyroxsulam, a cloquintocet salt, and a herbicide selected from florasulam, penoxsulam, diclosulam, cloransulam-methyl, flumetsulam, metosulam, and Compound A.

In some embodiments, the described compositions include pyroxsulam, a cloquintocet salt, and a herbicide selected from mesosulfuron, metsulfuron, thifensulfuron, tribenuron, triasulfuron, thiencarbazone, flucarbazone, flupyrsulfuron, and sulfosulfuron.

In some embodiments, the described compositions include pyroxsulam, a cloquintocet salt, and a herbicide selected from imazamox, imazapyr, and imazethapyr.

In some embodiments, the described compositions include pyroxsulam, a cloquintocet salt, and a herbicide selected from pinoxaden, clodinafop, fenoxyprop, and tralkoxydim.

In some embodiments, the described compositions include pyroxsulam, a cloquintocet salt, and a herbicide selected from pyrasulfotole, topramezone, and bicylopyrone.

In some embodiments, the pyroxsulam or an agriculturally acceptable salt thereof is provided in a premixed formulation with an additive. Exemplary premixes of pyroxsulam or an agriculturally acceptable salt thereof and an additive that are or have been commercially available include, but are not limited to, ADMITT®, CRUSADER®, QUASAR®, MERIT®, POWERFLEX®, SIMPLICITY®, ACROSS®, and BROADWAY® (trademarks of Dow AgroSciences, LLC).

In some embodiments, the compositions do not contain clopyralid or a salt thereof, 2,4-D or a salt thereof, halauxifen-methyl and a salt of CQC.

2. Adjuvants

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_9-C_{11} alkylpolyglycoside; phosphate alcohol ethoxylate; natural primary alcohol (C_{12}-C_{16}) 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.

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 dibutylnaphthalenesulfonic 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 Rhodamine 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.

3. Carriers

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 or less, 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 or less, esters of the above vegetable oils or less, 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 or less, 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.

VII. Methods of Use

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). 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.

A. Control of undesirable vegetation

In some embodiments, a method of controlling undesirable vegetation which comprises contacting the vegetation or the locus thereof with or applying to the soil or water to prevent the emergence or growth of vegetation 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 composition is applied postemergence to the undesirable vegetation.

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 disclosed herein are applied to vegetation or an area adjacent to the vegetation or applying to soil or water to prevent the emergence or growth of vegetation by spraying (e.g., foliar spraying). In some embodiments, the spraying techniques use, for example, water as carrier and spray liquor rates of from 2 liters per hectare (L/ha) to 2000 L/ha (e.g., from 10–1000 L/ha, or from 50–500 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 on the bare soil (e.g., post-directed or lay-by). In some embodiments, the compositions disclosed herein can be applied as dry formulations (*e.g.*, granules, DG's, etc.) into water.

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 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. Exemplary crops include, but are not limited to, wheat, barley, triticale, rye, teff, oats, corn, sorghum, rice, sugar cane and pasture grasses.

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 (CRP) lands, aquatics, 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.

B. Control of undesirable vegetation in resistant crops

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 compositions and methods described herein may be used to control undesirable vegetation in glyphosate-tolerant-, 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase inhibitor-tolerant-, glufosinate-tolerant-, glutamine synthetase inhibitor-tolerant-, dicamba-tolerant-, phenoxy auxin-tolerant-, pyridyloxy auxin-tolerant-, synthetic auxin-tolerant-, auxin transport inhibitor-tolerant-, aryloxyphenoxypropionate-tolerant-, cyclohexanedione-tolerant-, phenylpyrazoline-tolerant-, acetyl CoA carboxylase (ACCase) inhibitor-tolerant-, imidazolinone-tolerant-, sulfonylurea-tolerant-, pyrimidinylthiobenzoate-tolerant-, triazolopyrimidine-tolerant-, sulfonylaminocarbonyltriazolinone-tolerant-, acetolactate synthase (ALS) or acetohydroxy acid synthase (AHAS) inhibitor-tolerant-, 4-hydroxyphenyl-pyruvate dioxygenase (HPPD) inhibitor-tolerant-, phytoene desaturase inhibitor-tolerant-, carotenoid biosynthesis inhibitor-tolerant-,

protoporphyrinogen oxidase (PPO) inhibitor-tolerant-, cellulose biosynthesis inhibitor-tolerant-, mitosis inhibitor-tolerant-, microtubule inhibitor-tolerant-, very long chain fatty acid inhibitor-tolerant-, fatty acid and lipid biosynthesis inhibitor-tolerant-, photosystem I inhibitor-tolerant-, photosystem II inhibitor-tolerant-, triazine-tolerant- and bromoxynil-tolerant-crops (such as, but not limited to, soybean, cotton, canola/oilseed rape, rice, cereals, corn, sorghum, sunflower, sugar beet, sugarcane, turf, etc.), for example, in conjunction with glyphosate, EPSP synthase inhibitors, glufosinate, glutamine synthase inhibitors, dicamba, phenoxy auxins, pyridyloxy auxins, synthetic auxins, auxin transport inhibitors, aryloxyphenoxypropionates, cyclohexanediones, phenylpyrazolines, ACCase inhibitors, imidazolinones, sulfonylureas, pyrimidinylthiobenzoates, triazolopyrimidines, sulfonylaminocarbonyltriazolinones, ALS or AHAS inhibitors, HPPD inhibitors, phytoene desaturase inhibitors, carotenoid biosynthesis inhibitors, PPO inhibitors, cellulose biosynthesis inhibitors, mitosis inhibitors, microtubule inhibitors, very long chain fatty acid inhibitors, fatty acid and lipid biosynthesis inhibitors, photosystem I inhibitors, photosystem II inhibitors, triazines, and bromoxynil. The compositions and methods may be used in controlling undesirable vegetation in crops possessing multiple or stacked traits conferring tolerance to multiple chemistries and/or inhibitors of multiple modes of action. In some embodiments, the compositions described herein are 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. In some embodiments, the compositions described herein and other complementary herbicides are applied at the same time, either as a combination formulation or as a tank mix, or sequentially.

In some embodiments, the compositions and methods may be used in controlling undesirable vegetation in phenoxy acid tolerant crops, wherein the phenoxy acid tolerant crops have tolerance conferred by an AAD12 gene. In some examples, the compositions and methods may be used in controlling undesirable vegetation that is resistant to auxinic herbicides.

The compositions and methods may be used in controlling undesirable vegetation in crops possessing agronomic stress tolerance (including but not limited to drought, cold, heat, salt, water, nutrient, fertility, pH), pest tolerance (including but not limited to insects, fungi and pathogens) and crop improvement traits (including but not limited to yield; protein, carbohydrate, or oil content; protein, carbohydrate, or oil composition; plant stature and plant architecture).

C. Undesirable vegetation

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 convolvolus), 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, *Brassica* 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, *Sisymbrium* species, *Solanum* species, *Trifolium* species, *Xanthium* species, *Veronica* species, *Viola* species such as wild pansy(*Viola tricolor*), common chickweed *(Stellaria 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 annual gasses such as *Alopecurus* species, *Apera spica-venti*, *Avena* species such as wild oat (*Avena fatua*), *Bromus* species, *Lolium* species such as annual ryegrass (*Lolium multiflorum subsp. gaudini*), *Seteria* species, and *Panicum* species. In some examples, the undesirable vegetation is selected from the group consisting of wild oat (*Avena fatua*), annual ryegrass (*Lolium multiflorum subsp. gaudini*), and combinations thereof.

D. Application rates

The pyroxsulam, or an agriculturally acceptable salt thereof as described herein, can be used in an amount sufficient to induce a herbicidal effect. In some embodiments, the pyroxsulam or agriculturally acceptable salt thereof is applied to vegetation or an area adjacent to the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of 4 grams of active ingredient per hectare (g ai/ha) or greater (e.g., 6 g ai/ha or greater, 8 g ai/ha or greater, 10 g ai/ha or greater, 12 g ai/ha or greater, 14 g ai/ha or greater, 16 g ai/ha or

greater, 18 g ai/ha or greater, 20 g ai/ha or greater, 22 g ai/ha or greater, 24 g ai/ha or greater, 26 g ai/ha or greater, 28 g ai/ha or greater, 30 g ai/ha or greater, 32 g ai/ha or greater, 34 g ai/ha or greater, 36 g ai/ha or greater, or 38 g ai/ha or greater). In some embodiments, the pyroxsulam or agriculturally acceptable salt thereof is applied to vegetation or an area adjacent to the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of 40 g ai/ha or less (e.g., 38 g ai/ha or less, 36 g ai/ha or less, 34 g ai/ha or less, 32 g ai/ha or less, 30 g ai/ha or less, 28 g ai/ha or less, 26 g ai/ha or less, 24 g ai/ha or less, 22 g ai/ha or less, 20 g ai/ha or less, 18 g ai/ha or less, 16 g ai/ha or less, 14 g ai/ha or less, 12 g ai/ha or less, 10 g ai/ha or less, 8 g ai/ha or less, or 6 g ai/ha or less). In some embodiments, the pyroxsulam or agriculturally acceptable salt thereof is applied to vegetation or an area adjacent to the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of from 4–40 g ai/ha (e.g., from 6–30 g ai/ha, from 8–25 g ai/ha, or from 10–21 g ai/ha).

The cloquintocet salt described herein can be used in an amount sufficient to induce a safening effect on the pyroxsulam. In some embodiments, the cloquintocet salt is applied to vegetation or an area adjacent to the vegetation or applied to soil or water in an amount of 10 grams of acid equivalent per hectare (g ae/ha) or greater (e.g., 15 g ae/ha or greater, 20 g ae/ha or greater, 25 g ae/ha or greater, 30 g ae/ha or greater, 35 g ae/ha or greater, 40 g ae/ha or greater, 45 g ae/ha or greater, 50 g ae/ha or greater, 55 g ae/ha or greater, 60 g ae/ha or greater, 65 g ae/ha or greater, 70 g ae/ha or greater, or 75 g ae/ha or greater). In some embodiments, the cloquintocet salt is applied to vegetation or an area adjacent to the vegetation or applied to soil or water in an amount of 80 g ae/ha or less (e.g., 75 g ae/ha or less, 70 g ae/ha or less, 65 g ae/ha or less, 60 g ae/ha or less, 55 g ae/ha or less, 50 g ae/ha or less, 45 g ae/ha or less, 40 g ae/ha or less, 35 g ae/ha or less, 30 g ae/ha or less, 25 g ae/ha or less, 20 g ae/ha or less, or 15 g ae/ha or less). In some embodiments, the cloquintocet salt is applied to vegetation or an area adjacent to the vegetation or applied to soil or water to prevent the emergence or growth of vegetation in an amount of from 10–80 g ae/ha (e.g., from 20–75 g ae/ha, from 30–70 g ae/ha, or from 40–65 g ae/ha).

By way of non-limiting illustration, examples of certain embodiments of the present disclosure are given below. Parts and percentages are on a per weight basis unless otherwise indicated.

EXAMPLES

Example 1

Preparation and Analysis of Cloquintocet Salts

Thirteen cloquintocet acid (CQC) organoammonium salts were prepared: mono-, di- and triethanolammonium; mono-, di- and triisopropanolammonium; N,N-dimethylethanolammonium, choline, di- and triethylammonium; iso- and diisopropylammonium; and dimethylammonium. The ammonium and sodium salts of cloquintocet acid were also prepared.

A 10 wt% slurry of cloquintocet acid was prepared by adding the free acid (178.2 g ai; 0.75 mole) to a 3 L plastic beaker containing deionized water (1645 g) while stirring with an IKA stirrer fitted with a 1.5 inch saw tooth blade. A pH/temperature probe was fitted to the inside of the beaker and submersed in the slurry to monitor the solution pH and temperature during the base addition. The stirrer agitation speed was between 1000 and 1200 rpm. The base was added slowly via a disposable pipette to the slurry to slightly less than molar equivalence (99-99.5%). Complete solubilization of the free acid generally occurred between a pH of 5.5 to 6.0. The final solution pH of the salt solution concentrates was a nominal 6.5 ± 0.3. The only pH outlier was the triethanolammonium salt which had a neat solution pH of 6.0. Toward the end of the neutralization the 1% (wt) dilution pH was also measured. The two values were usually within 0.1-0.2 units of each other.

The exception to the above procedure occurred during the preparation of the ammonium salt. After the final ammonia addition, the solution gelled (taffy in appearance). The slurry was transferred to a 316 stainless steel beaker, additional water (572 g) was added, and the slurry was warmed to approximately 40 °C by means of a hot plate. A complete solution was obtained.

The sodium salt (comparative sample) was prepared via saponification of cloquintocet-mexyl with sodium hydroxide and water. The sodium salt solution was then transferred to a 316 stainless steel cake pan and placed in a forced air convection oven set between 70-80°C. Generally, 2 days were required to remove the excess water from the prepared CQC salts. After completion of drying, those salts that were solids were ground in a mortar and pestle and sieved thru a 14 mesh (1410 micron) screen.

The solidified salts were assayed for chemical purity and water content.

Isolation of the triethylammonium and N,N-dimethylethanolammonium salts by the above drying procedure resulted in poor accountability in terms of chemical assay and water.

This may have been caused by degradation during the isolation process. These two salts were prepared again as described above and then the excess water was removed via drying in a vacuum oven heated to a maximum of 50°C for approximately 2 days.

Chemical Assay and Water Analysis of the Described Cloquintocet Salts

The salts were assayed for cloquintocet acid via a high pressure liquid chromatography (HPLC) procedure and then the salt active ingredient was calculated from the acid equivalence. The results are reported as wt%. The water content of the solid cloquintocet salts was determined using the Karl Fisher (KF) method and reported as wt%. Chemical assay and water analysis were in line with the other salts which were 100 wt% ± 3 % for total accountability. The chemical assays for the salt active ingredient (ai) and water analysis are shown in Table 1. The majority of the salts showed a propensity to retain water.

Table 1. Chemical Assays of the Neat Cloquintocet Salts.

Salt	Salt MW	Acid equivalent	Chemical Assay, wt% ae	Calculated wt% ai	KF water, wt%	Calc. wt% ai + water
Monoethanolammonium	299	0.8	79	100	0.2	100
Diethanolammonium	343	0.7	68	98	2	100
Triethanolammonium	387	0.6	56	92	6	98
N,N-dimethylethanolammonium	327	0.7	73	100	2	103
Isopropanolammonium	313	0.8	73	96	2	99
Diisopropanolammonium	371	0.6	60	93	6	99
Triisopropanolammonium monohydrate	447	0.5	53	99	6	105
Diethylammmonium	311	0.8	72	94	8	101
Triethylammonium	339	0.7	66	95	9	103
Dimethylammonium	283	0.8	81	97	4	100
Isopropylammonium	298	0.8	80	101	1	102
Diisopropylammonium	339	0.7	67	95	5	100
Ammonium	255	0.9	91	98	2	100
Choline	341	0.7	62	88	10	98
Sodium	260	0.9	88	96	4	100

Measurement of the Water Solubility of the Described Cloquintocet Salts

A. Apparatus

A half jacketed 3-neck 500 ml glass flask connected to a circulation water temperature bath capable of maintaining the solution temperature to ± 0.1 °C was used. The center neck was fitted with a glass stirring rod connected to an IKA electric motor. A teflon rounded, paddle stirrer blade was attached to the rod. One of the outer necks was fitted with a thermometer calibrated to 0.1 °C. The other neck was fitted with a glass stopper and was used to withdraw a sample for analysis.

B. Procedure

1. The valve on the return line from the flask to the bath was first opened. The circulation bath was turned on. The temperature set point for the bath was set ~ 0.4-0.6°C below the desired temperature for the solution in the flask, i.e., 20.0°C. The flask was filled with 150 ml of DI water. The pH of the DI water was recorded. The stirrer rpm was slowly adjusted to 70-80 rpm.

2. The individual salt was slowly added through the open neck. A funnel was inserted into the neck to avoid collecting solids in the neck opening. The salt continued to be added until a slight excess of salt was visible in the solution. This required several hours in most cases depending on the salt's solubility. The amount of salt added was recorded. Using this value, the approximate salt concentration was calculated and provided as an approximate concentration.

3. Under continuous stirring the solution was sampled at the end of the day and the next morning by withdrawing approximately 2-3 ml using a disposable pipette. This solution was added to the open end of a 3 ml Lure-Lok Tip syringe fitted with a 0.2 μm Nylon Whatman filter. The plunger was then inserted into the syringe and the solution was filtered into a 7 ml glass vial. The vial was closed with non-aluminum lined cap. Samples were stored at laboratory ambient temperature until assayed.

The CQC salt water solubility data is shown in Table 2. Except for the ammonium and triethanolammonium salts, the CQC salts showed appreciable solubility at 20°C. CQC acid has a solubility of about 1.4 wt% in a pH 7 buffer solution. The diethanolammonium, isopropanolammonium and diisopropylammonium solubility data represents a minimum value since their solubility values do not reflect saturation. At the solubility levels reported, their solutions were viscous and difficult to sample.

Table 2. Water solubility (at 20°C) of cloquintocet salts.

Salt	Water Solubility wt% ae	AE	Calculated water solubility wt% ai	Neat pH	Density, g/mL
Monoethanolamine	26	0.8	33	6.3	1.1
Diethanolamine[1]	40	0.7	58	6.6	1.2
Triethanolamine[1]	9.2	0.6	15	6.1	1.0
Isopropanolamine[1]	31	0.8	41	7.4	1.1
Diisopropanolamine	30	0.6	46	6.4	1.1
Triisopropanolamine	36	0.5	50	6.4	1.1
Choline	31	0.7	45	6.8	1.1
N,N-dimethylethanolamine	36	0.7	36	5.7	1.1
Diethylamine	34	0.8	44	5.8	1.1
Triethylamine	19	0.7	27	5.6	1.1
Dimethylamine	40	0.8	48	6	1.2
Isopropylamine	31	0.8	38	5.7	1.1
Diisopropylamine	34	0.7	48	5.9	1.1
Ammonium	2.3	0.9	2.5	5.7	1.0
Acid[2]	1.4	1	1.4	5.6	1.0

[1]Minimum solubility due to high viscosity, [2]pH 7 buffer solution,

Example 2

Preparation of Representative Samples of the Herbicide Compositions Described Herein

Table 3. Representative Ingredient Amounts in the SC Herbicide Compositions Described Herein

Ingredient	Role	Amount (wt%)
pyroxsulam	active ingredient	0.1 - 10
herbicide 1[1]	active ingredient	0 - 20
herbicide 2[1]	active ingredient	0 - 20
cloquintocet salt	herbicide safener	2 - 20
silicone emulsion	antifoam	0.1 - 1
polymeric surfactant	wetter	1 - 10
anionic surfactant	dispersant	1 - 10
thickening gel	rheology additive	0.05 - 5
propylene glycol	antifreeze	1 - 10
water	solvent/diluent	30 - 90

[1] The compositions described herein may contain one or more additional herbicide active ingredients selected from the additive pesticide group described herein.

Sample 1. Pyroxsulam/CQC-TIPA SC

In the following order these ingredients were added to a 1 L plastic beaker with stirring: pyroxsulam (11.8 g, 97.1 wt%), cloquintocet-triisopropanolammonium (CQC-TIPA; 154.8 g, 15.5 wt% in water), 20 wt% Pluronic P105 in water (68.6 g), Polyfon H (13.7 g), propylene glycol (17.2 g), 1.5 % Kelzan ASX gel in water (29.2 g), 0.1 % Proxel GXL (0.25 g), Dow Corning Antifoam 1400 (0.65 g) and water (102.5 g). The blend was stirred under high shear using a Silverson L4R mixer for approximately 2 minutes. The slurry was then passed thru a wet mill at 5,000 rpm filled with 1-1.3 mm glass beads. After 2 passes the d(0.5) and d(0.9) particle sizes were 5.66 and 15.75 µm, respectively. The density of the suspension was 1.058 g/ml and the undiluted pH was 6.27. The chemical assay was 31 g/L of pyroxsulam and 63.2 g ae/L of cloquintocet-TIPA (114 g ai)/L. The complete composition of Sample 1 is shown in Table 4.

Table 4. Composition of Sample 1

Ingredient	Role	Amount (g/L)	Amount (wt%)
pyroxsulam[1]	active ingredient	31.0	2.93
cloquintocet-TIPA	herbicide safener	113.7	10.75
Dow Corning AF 1400	antifoam	1.7	0.16
Pluronic P105	wetter	36	3.4
Polyfon H	dispersant	36	3.4
Kelzan ASX	rheology additive	1.2	0.11
Proxel GXL	biocide	0.6	0.057
propylene glycol	antifreeze	45	4.25
water	solvent/diluent	793	74.93

Sample 2. Preparation of a Pyroxsulam/Halauxifen-methyl/CQC-TIPA Suspension Concentrate

Triisopropanolamine (TIPA; 27.0 g, 90% active) was added to 220 gram of water followed by powdered CQC acid (30.505 g). The mixture was mixed until all CQC acid solids dissolved. A first dispersant (2.5 g), a second dispersant (1.75 g), a wetting agent (0.45 g), pyroxsulam (14.68 g), halauxifen-methyl (5.14 g) and an antifoam agent (0.75 g) were then added to the above CQC-TIPA solution with overhead mixing. The mixture was wet-milled for 10 minutes @ 3800 rpm (particle size was measured: d(0.5) = 1.99 µm, d(0.9) = 6.06 µm, VMD = 2.85 µm). 53.39 g of water and 30 g of propylene glycol were then added to the wet-milled mixture, followed by addition of a first rheology additive stock solution (80 g, 5 wt% aqueous

solution), and a second rheology additive stock solution (33.33 g, 3 wt% aqueous solution). 0.5 g of Proxel GXL was added at the end. The mixture was mixed using overhead mixing with a Cowles disc. The composition of Sample 2 is shown in Table 5. The storage stability of sample 2 as determined using the Wet Sieve Test with a 325 mesh (45 μm) is shown in Table 6. The storage stability of sample 2 as determined using the particle size is shown in Table 7.

Table 5. Composition of Sample 2

Ingredient	Weight (g)	Weight %
halauxifen-methyl (97%)	5.14	1.000
pyroxsulam (97%)	14.68	2.850
cloquintocet acid (99%)	30.51	6.040
TIPA (90%)	27.00	4.860
first dispersant	2.50	0.500
second dispersant	1.75	0.35
wetter	0.45	0.090
antifoam	0.75	0.150
first rheology additive (5% in water)	80.00	0.800
second rheology additive (3% in water)	33.33	0.200
Proxel GXL	0.50	0.100
propylene glycol	30.00	6.000
water	273.39	77.060
Total	500.00	100.00

Table 6. Storage stability of Sample 2

	Time/Temperature	Wt% Solid Collected on Sieve
Wet Sieve Test 325 mesh (45 μm)	2-wks/54°C	0.00
	2-wks/FT	0.00
	2-wks/-10C	0.00
	2-wks/RT	0.00
	8-wks/40C	0.00

Table 7. Storage stability of Sample 2

	Time/Temperature	Particle Size
Particle Size d(0.5/0.9) in microns (µm)	2-wks/54°C	3.250/7.337
	2-wks/FT	3.558/8.007
	2-wks/-10C	3.406/7.720
	2-wks/RT	3.424/7.752
	8-wks/40C	3.264/7.370

Sample 3. Pyroxsulam/Clopyralid-monoethanololamine/Fluroxypyr-meptyl/CQC-monoethanololamine Suspoemulsion (aqueous suspension emulsion)

Using the ingredients shown in Table 8, a suspoemulsion composition containing clopyralid-monoethanolamine, fluroxypyr-meptyl, pyroxsulam and cloquintocet-monoethanolamine was prepared following general formulation preparative procedures.

Table 8. Composition of Sample 3

Ingredient	Concentration(g/L)	Concentration (wt%)
clopyralid-monoethanolamine	118.58	11.34
fluroxypyr-meptyl	129.68	12.4
pyroxsulam	12.8	1.22
cloquintocet acid	26.88	2.57
monoethanolamine	6.36	0.61
emulsifier 1	38.99	3.73
emulsifier 2	19.47	1.86
emulsion stabilizer	3.47	0.33
wetting agent	1.14	0.11
propylene glycol	37.75	3.61
rheology additive 1	0.28	0.0268
rheology additive 2	0.45	0.043
Proxel GXL	1.0	0.0956
antifoam	5.29	0.51
aromatic solvent	350.62	33.52
water	290.82	27.8
dispersant 1	2.09	0.20
dispersant 2	0.36	0.0344

Example 3

Evaluation of Eye Irritation Potential of Aqueous Solutions of the CQC Salts Using the Neutral Red Release (NRR) Assay

The purpose for this study was to conduct a preliminary investigation of the eye irritation potential of the more soluble CQC salt solutions using the *in vitro* Neutral Red Release (NRR) assay. The NRR assay is a screening assay designed to identify chemicals that have eye irritation potential. The assay is intended to identify chemicals that cause immediate cytotoxic damage to cell membranes. Specifically, the objective was to utilize this screening assay to quantitatively differentiate the CQC salts based on their eye irritation potential. A solution of CQC free acid was included for comparative purposes.

All materials were diluted (vol/vol; in phosphate buffered saline (PBS)) directly from the neat materials. Each test material was tested at eight concentrations, i.e., 0.5, 1, 2.5, 5, 7.5, 10, 60, 100% (vol/vol) and the concentration that resulted in release of 50% of preloaded neutral red (NR) dye (NRR50) compared to negative controls was determined. To enable appropriate interpretation and comparison across the salts, the NRR50 value for each test chemical was further corrected to its acid equivalent concentration (NRR50, mg ae/mL).

The NRR assay was performed in a 96-well format, with triplicate wells of each test material concentration for each assay. A total of two independent assay replicates were conducted on separate days. Sodium dodecyl sulfate (SDS; CAS # 151-21-3) at 5 mg/ml was used as the positive control and PBS as negative control.

Results for the positive control and the test material were evaluated relative to the criteria specified in the protocol. In the two independent assay replicates, the positive control compound, SDS, was positive, and the negative control, PBS, was negative, thereby demonstrating appropriate assay conduct.

The results of the NRR assay were used to calculate the NRR50 values for each CQC salt which were subsequently corrected for the CQC acid equivalent concentrations (NRR50, mg ae/mL). The corrected NRR50 mg ae/mL values were then ordered to facilitate relative comparison of eye irritation potential as defined by the NRR assay (Table 9). CQC salts with the highest NRR50 mg ae/mL values represent those with the lowest eye irritation potential. The NRR assay results when corrected to the acid equivalent basis for each salt indicated a broad range of values ranging from 3 to 213 mg ae/ml. Of the tested salts, CQC-choline possessed the highest NRR50, mg ae/mL value of 213, followed by CQC diethanolamine (NRR50, 92 mg

ae/mL), whereas, CQC-ammonium and CQC-acid had the lowest NRR50 mg ae/mL (3 and 9, respectively) which indicates they possess the highest eye irritation potential.

Table 9. NRR50 (mg ae/mL) Values for the CQC Salts Described Herein

CQC Salt	g ae/mL	AE	NRR50 (%v/v)	NRR50, mg ae/mL[1]	Relative Potential Eye Irritancy
Choline	0.354	0.697	60	213	lowest
Diethanolamine	0.484	0.693	19	92	
Isopropanolamine	0.350	0.76	15.6	55	
Dimethylamine[2]	0.102/ 0.463	0.841	25,11.4, 4.5	25.5, 53, 21(ave=33)	
Monoethanolamine	0.299	0.794	17.1	51	
Triisopropanolamine	0.298	0.532	6.6, 7.7	20, 23	
N,N-dimethylethanolamine	0.290	0.727	6.8, 6.8	20, 20	
Isopropylamine	0.339	0.798	5.6	19	
Diethylamine	0.381	0.765	3.9	15	
Acid	0.010	1.0	88.7	9	
Ammonium	0.023	0.933	13.4	3	highest

[1]NRR50, mg ae/mL = (1000*g ae/mL)×(NRR50/100);
[2]Two concentrations of CQC-dimethylammonium were tested.

Example 4

Evaluation of Eye Irritation Potential of Aqueous Herbicide Suspension Concentrates Containing Cloquintocet Salts

The eye irritation potential of the following CQC salt/aqueous pyroxsulam suspension concentrates (SC) formulations were measured utilizing the NRR assay: CQC-choline, CQC - diethanolammonium, CQC-isopropylammonium, CQC-dimethylammonium, and CQC-triisopropanolammonium. These CQC salts were identified to possess low eye irritation potential in Example 2 and showed high water solubility.

All of the selected test materials (salts and formulations) were tested at the following concentrations: 1.6, 3.1, 6.3, 12.5, 25, 50, 75 and 100% (neat as provided) and the concentration of the test material that resulted in release of 50% (NRR50) of preloaded NR dye compared to

negative controls was determined. To enable appropriate interpretation, NRR50 value for each test substance was further corrected to their CQC acid equivalent concentration (NRR50, mg ae/mL).

The NRR assay was performed in a 96-well format, with triplicate wells of each test material concentration for each assay. A total of two independent assay replicates were conducted on separate days. Sodium dodecyl sulfate (SDS; CAS # 151-21-3) at 5 mg/ml was used as the positive control and PBS as negative control. The dispersant Polyfon H and wetting agent Pluronic P-105 were used in the SC compositions at concentrations of 36 and 20 g ai/L, respectively.

The results shown in Table 10 indicate that CQC salt containing herbicide formulations differ in their eye irritation potential as defined by the NRR assay. Specifically, the results indicate that the formulations containing the various CQC-salts exhibited NRR50 mg ae/mL values that ranged from 113-3. The relative order of eye irritation potential for these herbicide formulations closely followed the order of eye irritation potential for the individual CQC salts shown in Table 9.

Table 10. NRR50 Values for Pyroxsulam/CQC Salt Containing Formulations Described Herein

Formulation Pyroxsulam + CQC Salt	Pyroxsulam mg ai/mL	CQC mg ae/mL	NRR50 (%v/v)	NRR50 mg ae/mL[1]
CQC-Choline	90	198	57	113
CQC-diethanolammonium	93	194	47	91
CQC-isopropanolammonium	89	192	29	56
CQC-dimethylammonium	92	191	22	41
CQC-TIPA Trial 1[2]	30	63	>100	>63
CQC-TIPA Trial 2	30	63	61	39
CQC- monoethanolammonium	31	62	79	49
CQC-dimethylethanolammonium	31	62	18	11
CQC-isopropylammonium	31	62	29.5	18
CQC-diethylammonium	31	62	14	9
CQC-ammonium	31	63	5	3

[1]NRR50, mg ae/mL CQC-salt = (CQC mg ae/mL)×(NRR50/100);

[2] In Trial 1, the 100% test sample afforded only a 48.5% NRR value.

Example 5

Herbicide Biology - Greenhouse Evaluation of the Described Compositions

Plant Propagation

A peat based potting soil, Metro-mix 360, (produced by Sun Gro Horticulture Canada CM Ltd) was used as the soil media for this test. Metro-mix 360 is a growing medium consisting of Canadian sphagnum peat moss, coarse perlite, bark ash, starter nutrient charge (with gypsum) and slow release nitrogen and dolomitic limestone. Several seeds of each crop or weed species were planted in 10 cm square pots and top watered twice daily. Plant material was propagated in greenhouse zone E2 at temperatures ranging from 18 to 20°C and 50 to 60% relative humidity. Natural light was supplemented with 1000-watt metal halide overhead lamps with an average illumination of 500 microeinsteins per square meter per second ($\mu E\ m^{-2}\ s^{-1}$) photosynthetic active radiation (PAR). Day length was 16 hours. Plant material was top-watered prior to treatment and sub-irrigated after treatment.

Herbicide Application

Herbicides were applied with a track sprayer manufactured by Allen Machine Works and located in building 306, room E1-483, at the Dow AgroSciences Indianapolis, Indiana Global Headquarters site (9330 Zionsville Road, Indianapolis, Indiana, USA). The track sprayer was calibrated to deliver 50 L/ha at 40 psi (262 kPa) pressure utilizing an 8001E even flat fan nozzle tip with a speed of 1.6 mph (2.6 km/h). The nozzle height was 46 cm above the plant canopy. Appropriate amounts of formulated product were added to vials as calculated by the software package ARM8 (Gylling Data Management Inc.). The vials contained a pH 7 phosphate buffer (Fischer Scientific) and the herbicide aliquots were diluted to a total volume of 60 ml. The growth stage of the crop and weed species at application was 2 to 4 leaf (Table 11). The application rates were 0, 17.8 and 37.6 g ai/ha of pyroxsulam for crop tolerance comparisons and 0, 2.35 and 4.7 g ai/ha of pyroxsulam for weed control comparisons. Cloquintocet was applied at a 1:2.1 ratio of pyroxsulam (g ai) : cloquintocet (g ae) in all treatments containing the safener. Treatments were replicated 4 times. Plants were returned to the greenhouse after treatment and sub-watered throughout the duration of the experiment. Plant material was fertilized twice weekly with Hoagland's fertilizer solution that is readily available in the greenhouses. Percent visual injury assessments were made on a scale of 0 to 100% as compared to the untreated control plants (where 0 is equal to no injury and 100 is equal to complete death of the plant.

Table 11. Growth stage of plant species tested

Common Name	Scientific Name	EPPO Code	Growth Stage at Application
Spring wheat	*Triticum aestivum*	TRZAS	3 to 4 leaves
Durum wheat	*Triticum durum*	TRZDU	3 to 4 leaves
Wild Oats	*Avena fatua*	AVEFA	2 to 3 leaves

Evaluation of Cloquintocet Salts to Safen Pyroxsulam on Crops

Pyroxsulam was tested with various cloquintocet salts for their ability to reduce injury to grass crops. Visual determination of injury on spring wheat (*Triticum aestivum L.*, **TRZAS**) and durum wheat (*Triticum durum L.* **TRZDU**) from spray treatments with pyroxsulam alone and with several forms of cloquintocet was conducted. All forms of cloquintocet were applied at a 1:2.1 weight ratio of pyroxsulam:cloquintocet (AE). Results are shown in Table 12.

Table 12. Ability of Cloquintocet Salts to Safen Pyroxsulam to Spring and Durum Wheat

Pyroxsulam Rate (g ai/ha)	Cloquintocet form	TRZAS Injury 22 DAA (% Injury)	TRZDU Injury 22 DAA (% Injury)
18.8	No safener	70	82
37.6	No safener	76	88
18.8	mexyl	3	19
37.6	mexyl	15	34
18.8	acid	0	4
37.6	acid	25	26
18.8	choline	6	9
37.6	choline	21	12
18.8	diethanolamine	18	12
37.6	diethanolamine	21	18
18.8	isopropanolamine	2	9
37.6	isopropanolamine	20	12
18.8	dimethylamine	11	9
37.6	dimethylamine	11	15
18.8	monoethanolamine	1	10
37.6	monoethanolamine	14	19
18.8	triisopropanolamine	4	11
37.6	triisopropanolamine	9	24
18.8	isopropylamine	2	8
37.6	isopropylamine	20	14
18.8	diethylamine	5	12
37.6	diethylamine	15	18

Evaluation of Various Pyroxsulam + Cloquintocet Salt Treatments to Control Weeds

Visual determination of the control of wild oats (*Avena fatua L.*, **AVEFA**) treated with pyroxsulam alone and with several forms of cloquintocet was conducted. All forms of cloquintocet were applied at a 1:2.1 weight ratio of pyroxsulam: cloquintocet (AE). Results are shown in Table 13.

Table 13. Ability of Cloquintocet/Pyroxsulam Compositions to Control Wild Oats

Pyroxsulam Rate (g ai/ha)	Cloquintocet form	AVEFA Control 21 DAA (% Control)
2.35	No safener	86
4.7	No safener	98
2.35	mexyl	71
4.7	mexyl	84
2.35	acid	96
4.7	acid	99
2.35	choline	94
4.7	choline	99
2.35	diethanolamine	88
4.7	diethanolamine	94
2.35	isopropanolamine	80
4.7	isopropanolamine	90
2.35	dimethylamine	88
4.7	dimethylamine	90
2.35	monoethanolamine	91
4.7	monoethanolamine	99
2.35	triisopropanolamine	97
4.7	triisopropanolamine	96
2.35	isopropylamine	90
4.7	isopropylamine	99
2.35	diethylamine	88
4.7	diethylamine	99

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 or less, 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 herbicidally effective amount of (a) pyroxsulam or an agriculturally acceptable salt thereof and (b) a cloquintocet salt, wherein the cloquintocet salt comprises a cation of the formula $N(R^1)(R^2)(R^3)(R^4)^+$, wherein R^1, R^2, R^3, and R^4 are independently H, C_1-C_4 alkyl, or C_1-C_4 hydroxyalkyl.

2. The composition of claim 1, wherein the cloquintocet salt comprises a cation selected from the group consisting of monoethanolammonium, diethanolammonium, triethanolammonium, monoisopropanolammonium, diisopropanolammonium, triisopropanolammonium, choline, N,N-dimethylethanolammonium, diethylammonium, dimethylammonium, isopropylammonium, or mixtures thereof.

3. The composition of claim 2, wherein the cloquintocet salt comprises a cation selected from the group consisting of monoethanolammonium, diethanolammonium, monoisopropanolammonium, choline, dimethylammonium, triisopropanolammonium, or mixtures thereof.

4. The composition of claim 3, wherein the cloquintocet salt comprises a cation selected from the group consisting of monoethanolammonium, choline, dimethylammonium, triisopropanolammonium, or mixtures thereof.

5. The composition of any one of claims 1-4, wherein the composition is an aqueous suspension concentrate.

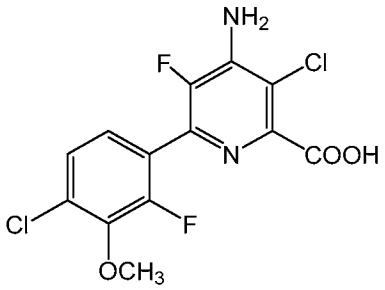
6. The composition of any one of claims 1-4, wherein the composition is an aqueous suspension emulsion concentrate.

7. The composition of any one of claims 1-4, wherein the composition is a water-soluble granule or a water-dispersible granule.

8. The composition of any one of claims 1-7, wherein the weight ratio of (a) in g ai/ha to (b) in g ae/ha is from about 1:4 to about 1:0.5.

9. The composition of any one of claims 1-8, further comprising an additional pesticide.

10. The composition of claim 9, wherein the additional pesticide is selected from the group including aminopyralid, clopyralid, florasulam, fluroxypyr-meptyl, halauxifen-methyl, penoxsulam, and the compound of formula



or a C_1-C_{12} alkyl or C_7-C_{12} arylalkyl ester or salt thereof.

11. The composition of claim 9, wherein the additional pesticide is selected from the group consisting of cloransulam-methyl, diclosulam, flumetsulam, isoxaben, metosulam, 2,4-D, MCPA, picloram, propyzamide, triclopyr, tebuthiuron, thiazopyr, and trifluralin.

12. A method of controlling undesirable vegetation which comprises contacting the vegetation or the locus thereof with or applying to the soil or water to prevent the emergence or growth of vegetation the composition of any one of claims 1-11.

13. The method of claim 12, wherein the composition is applied postemergence to the undesirable vegetation.

14. The method of claim 12 or 13, wherein the undesirable vegetation is controlled in wheat, barley, triticale, teff, oats, sorghum, corn, rice, sugarcane, or pasture grasses.

15. The method of claim 14, wherein the undesirable vegetation is controlled in wheat.

16. The method of claim 14 or 15, wherein the undesirable vegetation is controlled in glyphosate-, 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase inhibitor-, glufosinate-, glutamine synthetase inhibitor-, dicamba-, phenoxy auxin-, pyridyloxy auxin-, synthetic auxin-, auxin transport inhibitor-, aryloxyphenoxypropionate-, cyclohexanedione-, phenylpyrazoline-, acetyl CoA carboxylase (ACCase) inhibitor-, imidazolinone-, sulfonylurea-, pyrimidinylthiobenzoate-, triazolopyrimidine-, sulfonylaminocarbonyltriazolinone-, acetolactate synthase (ALS) or acetohydroxy acid

synthase (AHAS) inhibitor-, 4-hydroxyphenyl-pyruvate dioxygenase (HPPD) inhibitor-, phytoene desaturase inhibitor-, carotenoid biosynthesis inhibitor-, protoporphyrinogen oxidase (PPO) inhibitor-, cellulose biosynthesis inhibitor-, mitosis inhibitor-, microtubule inhibitor-, very long chain fatty acid inhibitor-, fatty acid and lipid biosynthesis inhibitor-, photosystem I inhibitor-, photosystem II inhibitor-, triazine-, or bromoxynil- tolerant crops.

17. The method of claim 16, wherein the undesirable vegetation is controlled in phenoxy acid tolerant crops and the phenoxy acid tolerant crops have tolerance conferred by an AAD12 gene.

18. The method of any one of claims 12-17, wherein the undesirable vegetation is resistant to auxinic herbicides.

19. The method of any one of claims 12-18, wherein the undesirable vegetation is selected from the group consisting of wild oat, annual ryegrass, and combinations thereof.

20. The method of any one of claims 12-19, wherein (a) is applied in an amount of from 4-40 g ai/ha.

21. The method of any one of claims 12-20, wherein (b) is applied in an amount of from 10-80 g ae/ha.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/13123

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.: 8-21
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.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/13123

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A01N 43/40, A01N 43/90, A01N 43/42 (2017.01)
CPC - A01N 25/32, A01N 43/42, A01N 43/40
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 43/40, A01N 43/90, A01N 43/42 (2017.01)
CPC: A01N 25/32, A01N 43/42, A01N 43/40

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)
PatBase; Keyword limited: pyroxsulam; cloquintocet/salt; mono/di/triethanolammonium; mono/di/triisopropanolammonium; choline; N,N dimethylethanolammonium; herbicidal composition; herbicidally effective amount.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013/0217578 A1 (HARE) 22 August 2013 (22.08.2013), entire document, especially: para [0004]; para [0019].	1-7
Y	US 2014/0100109 A1 (SATCHIVI et al.) 10 April 2014 (10.04.2014), entire document, especially: para [0010]; para [0013]; para [0019]; pg 7-8, Tables 5, 6, 7, and 8.	1-7
A	US 2014/0179526 A1 (HOPKINS) 26 June 2014 (26.06.2014), entire document.	1-7
A	US 2012/0238449 A1 (MANN) 20 September 2012 (20.09.2012), entire document.	1-7

☐ 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
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 March 2017	06 APR 2017
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 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)