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(71) Applicant: **FMC CORPORATION** [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US).

(72) Inventors: **LUMBER, Stuart**; 88/1152 Sukhumvit Soi 49, Klongton Jua, Wattana, Bangkok, 10110 (TH). **NORTH, Dugald, C.r.**; 31 Norman Terrace, Enoggera, Queensland, 4051 (AU).

(74) Agents: **SMALL, Andrea, D.** et al.; FMC Corporation, 1735 Market Street, Philadelphia, PA 19103 (US).

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(54) Title: METHODS FOR SELECTIVELY CONTROLLING PLANTS USING COMPOSITIONS CONTAINING PHOTOSYSTEM II INHIBITORS AND PROTOPORPHYRINOGEN OXIDASE INHIBITORS

(57) Abstract: Methods for the selective control of a plant in the *Brassicaceae family* in a cereal crop that include the steps of applying to the *Brassicaceae* plant a herbicidally effective amount of a composition that includes (a) a photosystem II inhibitor and (b) a protoporphyrinogen oxidase inhibitor are presented.

METHODS FOR SELECTIVELY CONTROLLING PLANTS USING COMPOSITIONS CONTAINING PHOTOSYSTEM II INHIBITORS AND PROTOPORPHYRINOGEN OXIDASE INHIBITORS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority of U.S. Provisional Application No. 61/972,457 filed on March 31, 2014, the disclosure of which is incorporated by reference in its entirety.

FIELD OF THE DISCLOSED SUBJECT MATTER

The presently disclosed subject matter relates to compositions that include photosystem II inhibitors and protoporphyrinogen oxidase inhibitors, and methods for controlling plants using those compositions.

BACKGROUND

One of the more preferred methods of controlling weeds in crops involves the post-emergent control of weeds wherein herbicide(s) are applied after the crop in question has emerged from the soil. Post-emergent control is desirable as it requires the application of herbicide only where an infestation of weeds is present.

Photosystem II inhibitors are herbicides that reduce electron flow from water to NADPH2+ at the photochemical step in photosynthesis. They bind to the Qb site on the D1 protein, and prevent quinone from binding to this site. Therefore, this group of compounds causes electrons to accumulate on chlorophyll molecules. As a consequence, oxidation reactions in excess of those normally tolerated by the cell occur, the cells die, and ultimately the plant dies.

Protoporphyrinogen oxidase inhibitors are herbicides that act by blocking the production of chlorophyll and heme in the plant, and causing an accumulation of protoporphyrinogen that is ultimately toxic to the plant.

In recent years, however, as a result of the continued use of the same kinds of herbicides over so many years, herbicide resistant weeds are becoming an increasing problem. Accordingly, a need exists for herbicidal compositions and methods exhibiting high activity and effectiveness against such resistant weeds.

SUMMARY OF THE DISCLOSED SUBJECT MATTER

In one embodiment, the present disclosure provides a method for the selective control of a plant in the *Brassicaceae family* in a cereal crop that includes the step of applying to the *Brassicaceae* plant a herbicidally effective amount of a composition that includes (a) a photosystem II inhibitor and (b) a protoporphyrinogen oxidase inhibitor. In one embodiment, the composition is applied at a rate of about 10 g ai/acre to about 500g ai/acre. In another embodiment, the composition is applied at a rate of about 50 g ai/acre to about 120 g ai/acre.

In one embodiment, the cereal crop is selected from wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio.

In another embodiment, the composition includes (a) a photosystem II inhibitor and (b) a protoporphyrinogen oxidase inhibitor in a formulation selected from water dispersible granular formulations, emulsion concentrates, suspension concentrates, suspo-emulsions, capsule suspensions, emulsifiable granules, water in oil emulsions, oil in water emulsions, micro-emulsions, oil dispersions, oil miscible flowables, oil miscible liquids, soluble concentrates, ultra-low volume suspensions, ultra-low volume liquids, dispersible concentrates, and wettable powders.

In an embodiment, the photosystem II inhibitor is selected from ametryn, atrazine, cyanazine, hexazinone, metribuzin, and simazine.

In another embodiment, the protoporphyrinogen oxidase inhibitor is selected from acifluorfen-sodium, bifenox, chlomethoxyfen, chlornitrofen, ethoxyfen-ethyl, fluorodifen, fluoroglycofen-ethyl, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen, oxyfluorfen, cinidon-ethyl, flumiclorac-pentyl, flumioxazine, profluazol, pyrazogyl, oxadiargyl, oxadiazon, pentoxazone, fluazolate, pyraflufen-ethyl, benzfendizone, butafenacil, fluthiacet-methyl, thidiazimin, azafenidin, carfentrazone-ethyl, sulfentrazone, and flufenpyr-ethyl.

In one embodiment, the plant in the *Brassicaceae* family includes *Raphanus raphanistrum*.

Another aspect of the disclosure is directed to a method for the selective control of the plant *Raphanus raphanistrum* in a cereal crop, comprising applying to the *Raphanus raphanistrum* a herbicidally effective amount of a composition comprising (a) metribuzin, and (b) carfentrazone-ethyl. In one embodiment of the method, the composition is applied at a rate of about 10 g ai/acre to about 500g ai/acre; preferably at a rate of about 50 g ai/acre to

about 120 g ai/acre. In one embodiment of the method, the cereal crop is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio.

Yet another aspect of the disclosure is directed to a composition for selectively controlling the plant *Raphanus raphanistrum* in a cereal crop, said composition comprising carfentrazone-ethyl and a photosystem II inhibitor in a ratio of about 1:4 to about 1:20 by weight, which selectively controls the plant *Raphanus raphanistrum* in a cereal crop. In one embodiment of the composition, the photosystem II inhibitor is selected from the group consisting of ametryn, atrazine, cyanazine, hexazinone, metribuzin, and simazine; preferably the photosystem II inhibitor is metribuzin. In one embodiment the composition contains carfentrazone-ethyl and metribuzin in a ratio of about 1:4.2. In one embodiment of the composition, the cereal crop is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio. In one embodiment the composition is in the form of a suspension concentrate.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present document discloses methods that provide synergistic efficacy for controlling plants in the *Brassicaceae family*. This plant family includes one of the most problematic weeds in Australian agriculture, the wild radish (*Raphanus raphanistrum*). The methods disclosed in this document are advantageous in that this combination now provides a new tool to control weeds in this family which are now resistant to many of the commonly-used herbicidal groups.

The compositions of this disclosure include combinations of two herbicides, a protoporphyrinogen oxidase inhibitor and a photosystem II inhibitor. In one embodiment, the ratio of protoporphyrinogen oxidase inhibitor to photosystem II inhibitor ranges from about 1:2 to about 1:60 by weight (or any specific ratio within this range), preferably from about 1:2 to about 1:35 by weight and most preferred from about 1:4 to about 1:20 by weight. These can be commercial formulations that are tank mixed at the time of application, or more preferably, a suspension concentrate premix formulation.

In one embodiment of this invention, photosystem II inhibitors include, but are not limited to, ametryn, atrazine, cyanazine, hexazinone, metribuzin, and simazine. In a preferred embodiment of this invention, the photosystem II inhibitor is metribuzin.

In another embodiment of this invention, protoporphyrinogen oxidase inhibitors include, but are not limited to, acifluorfen-sodium, bifenox, chlomethoxyfen, chlornitrofen, ethoxyfen-ethyl, fluorodifen, fluoroglycofen-ethyl, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen, oxyfluorfen, cinidon-ethyl, flumiclorac-pentyl, flumioxazine, profluazol, pyrazogyl, oxadiargyl, oxadiazon, pentoxazone, fluazolate, pyraflufen-ethyl, benzfendizone, butafenacil, fluthiacet-methyl, thidiazimin, azafenidin, carfentrazone-ethyl, sulfentrazone, flufenpyr-ethyl, as well as other protoporphyrinogen oxidase -inhibiting compounds, and their agriculturally-acceptable salts, esters, acids, and metabolites. In a preferred embodiment, the protoporphyrinogen oxidase inhibitor is carfentrazone-ethyl.

The compositions of the present disclosure can be in any conventional agriculturally useful form, for example, in the form of a twin pack, or in a ready-to-use formulation, or in the form of a tank mix. Additionally, the active compounds can be supplied (either separately or pre-mixed) in any appropriate formulation type, for example an emulsion concentrate (EC), a suspension concentrate (SC), a suspo-emulsion (SE), a capsule suspension (CS), a water dispersible granule (WG), an emulsifiable granule (EG), a water in oil emulsion (EO), an oil in water emulsion (EW), a micro-emulsion (ME), an oil dispersion (OD), an oil miscible flowable (OF), an oil miscible liquid (OL), a soluble concentrate (SL), an ultra-low volume suspension (SU), an ultra-low volume liquid (UL), a dispersible concentrate (DC), a wettable powder (WP), a mixed heterogeneous formulation of CS and EW (ZW), or any other technically feasible formulation in combination with agriculturally acceptable adjuvants. For tank mixing, commercial formulations of a photosystem II inhibitor and a protoporphyrinogen oxidase inhibitor are combined in a tank prior to application, in the appropriate ratio to provide the targeted weight ratio of the active ingredients. In one preferred embodiment, the compositions of the present disclosure are supplied as premix suspension concentrates.

The compositions and tank mixes of the present disclosure are useful for the control of plants in the *Brassicaceae* family in cereal crops. In one embodiment, cereal crops include, but are not limited to, wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio. In a preferred embodiment, cereal crops include wheat and barley.

Plants in the *Brassicaceae* family include, but are not limited to, *Raphanus raphanistrum*.

Rates of application of the composition, or tank-mixed separately formulated active ingredients, will vary according to prevailing conditions such as targeted plants, degree of

infestation, weather conditions, soil conditions, crop species, mode of application, and application time. Compositions containing a photosystem II inhibitor and a protoporphyrinogen oxidase inhibitor can be applied as sprays, such as water-dispersible concentrates, wettable powders, or water-dispersible granules. In one embodiment, the rate of application for active ingredient ("ai") (e.g. a photosystem II inhibitor and a protoporphyrinogen oxidase inhibitor) is from about 10 g ai/acre to about 500g ai/acre, preferably about 50 g ai/acre to about 120 g ai/acre.

The compositions and tank mixes of the present disclosure can additionally comprise further crop protection agents. The compositions and tank mixes of the present disclosure can additionally comprise further crop protection agents. Suitable crop protection active ingredients for the formulations of the present disclosure include the following:

Insecticides: A1) the class of carbamates consisting of aldicarb, alanycarb, benfuracarb, carbaryl, carbofuran, carbosulfan, methiocarb, methomyl, oxamyl, pirimicarb, propoxur and thiodicarb; A2) the class of organophosphates consisting of acephate, azinphos-ethyl, azinphos-methyl, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidaphos, methidathion, mevinphos, monocrotophos, oxymethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, pirimiphos-methyl, quinalphos, terbufos, tetrachlorvinphos, triazophos and trichlorfon; A3) the class of cyclodiene organochlorine compounds such as endosulfan; A4) the class of fiproles consisting of ethiprole, fipronil, pyrafluprole and pyriprole; A5) the class of neonicotinoids consisting of acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid and thiamethoxam; A6) the class of spinosyns such as spinosad and spinetoram; A7) chloride channel activators from the class of mectins consisting of abamectin, emamectin benzoate, ivermectin, lepimectin and milbemectin; A8) juvenile hormone mimics such as hydroprene, kinoprene, methoprene, fenoxycarb and pyriproxyfen; A9) selective homopteran feeding blockers such as pymetrozine, flonicamid and pyrifluquinazon; A10) mite growth inhibitors such as clofentezine, hexythiazox and etoxazole; A11) inhibitors of mitochondrial ATP synthase such as diafenthiuron, fenbutatin oxide and propargite; uncouplers of oxidative phosphorylation such as chlorfenapyr; A12) nicotinic acetylcholine receptor channel blockers such as bensultap, cartap hydrochloride, thiocyclam and thiosultap sodium; A13) inhibitors of the chitin biosynthesis type 0 from the benzoylurea class consisting of bistrifluron, diflubenzuron, flufenoxuron, hexaflumuron, lufenuron, novaluron and

teflubenzuron; A14) inhibitors of the chitin biosynthesis type 1 such as buprofezin; A15) moulting disruptors such as cyromazine; A16) ecdyson receptor agonists such as methoxyfenozide, tebufenozide, halofenozide and chromafenozide; A17) octopamin receptor agonists such as amitraz; A18) mitochondrial complex electron transport inhibitors pyridaben, tebufenpyrad, tolfenpyrad, flufenerim, cyenopyrafen, cyflumetofen, hydramethylnon, acequinocyl or fluacrypyrim;A19) voltage-dependent sodium channel blockers such as indoxacarb and metaflumizone; A20) inhibitors of the lipid synthesis such as spirodiclofen, spiromesifen and spirotetramat; A21) ryanodine receptor-modulators from the class of diamides consisting of flubendiamide, the phthalamide compounds (R)-3-Chlor-N1-{2- methyl-4-[1,2,2,2-tetrafluor-1-(trifluormethyl)ethyl]phenyl}-N2-(1-methyl-2-methylsulfonylethyl)phthalamid and (S)-3-Chlor-N1-{2-methyl-4-[1,2,2,2-tetrafluor-1-(trifluormethyl)ethyl]phenyl}-N2-(1- methyl-2-methylsulfonylethyl)phthalamid, chloranthraniliprole and cyanthraniliprole; A22) compounds of unknown or uncertain mode of action such as azadirachtin, amidoflumet, bifenazate, fluensulfone, piperonyl butoxide, pyridalyl, sulfoxaflor; or A23) sodium channel modulators from the class of pyrethroids consisting of acrinathrin, allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, tau-fluvalinate, permethrin, silafluofen and tralomethrin.

Fungicides: B1) azoles selected from the group consisting of bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, enilconazole, epoxiconazole, fluquinconazole, fenbuconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, simeconazole, triadimefon, triadimenol, tebuconazole, tetraconazole, triticonazole, prochloraz, pefurazoate, imazalil, triflumizole, cyazofamid, benomyl, carbendazim, thiabendazole, fuberidazole, ethaboxam, etridiazole and hymexazole, azaconazole, diniconazole-M, oxpoconazol, paclobutrazol, uniconazol, 1-(4-chlorophenyl)-2-([1,2,4]triazol-1-yl)-cycloheptanol and imazalilsulfphate; B2) strobilurins selected from the group consisting of azoxystrobin, dimoxystrobin, enestroburin, fluoxastrobin, kresoxim-methyl, methominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, trifloxystrobin, enestroburin, methyl (2-chloro-5-[1-(3-methylbenzyloxyimino)ethyl]benzyl)carbamate, methyl (2-chloro-5-[1-(6-methylpyridin-2-ylmethoxyimino)ethyl]benzyl)carbamate and methyl 2-(ortho-(2,5-dimethylphenyloxymethylene)- phenyl)-3-methoxyacrylate, 2-(2-(6-(3-chloro-2-methyl-phenoxy)-5-fluoro-pyrimidin-4-yloxy)-phenyl)-2-methoxyimino-N-methyl-acetamide and 3-

methoxy-2-(2-(N-(4-methoxy-phenyl)-cyclopropanecarboximidoylsulfanylmethyl)-phenyl)-acrylic acid methyl ester; B3) carboxamides selected from the group consisting of carboxin, benalaxyl, benalaxyl-M, fenhexamid, flutolanil, furametpyr, mepronil, metalaxyl, mefenoxam, ofurace, oxadixyl, oxycarboxin, penthiopyrad, isopyrazam, thifluzamide, tiadinil, 3,4-dichloro-N-(2-cyanophenyl)isothiazole-5-carboxamide, dimethomorph, flumorph, flumetover, fluopicolide (picobenzamid), zoxamide, carpropamid, diclocymet, mandipropamid, N-(2- (4-[3-(4-chlorophenyl)prop-2-ynyloxy]-3-methoxyphenyl)ethyl)-2-methanesulfonyl-amino-3-methylbutyramide, N-(2-(4-[3-(4-chlorophenyl)prop-2-ynyloxy]-3-methoxy-phenyl)ethyl)-2-ethanesulfonylamino- 3-methylbutyramide, methyl 3-(4-chlorophenyl)-3-(2-isopropoxycarbonyl- amino-3-methyl-butyrylamino)propionate, N-(4'-bromobiphenyl-2-yl)-4-difluoromethyl-methylthiazole-δ-carboxamide, N-(4'-trifluoromethyl-biphenyl-2-yl)-4-difluoromethyl-2-methylthiazole-5-carboxamide, N-(4'- chloro-3'-fluorobiphenyl-2-yl)-4-difluoromethyl-2-methyl-thiazole-5-carboxamide, N-(3,4'-dichloro-4-fluorobiphenyl-2-yl)-3-difluoro-methyl-1-methyl-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazole-4-carboxamide, N-(2-cyano-phenyl)- 3,4-dichloroisothiazole-5-carboxamide, 2-amino-4-methyl-thiazole-5-carboxanilide, 2-chloro-N-(1,1,3-trimethyl-indan-4-yl)-nicotinamide, N-(2-(1,3-dimethylbutyl)-phenyl)-1,3-dimethyl-5-fluoro-1 H-pyrazole-4-carboxamide, N-(4'-chloro-3',5-difluoro-biphenyl-2-yl)-3-difluoromethyl-1-methyl-I H-pyrazole-4-carboxamide, N-(4'-chloro-3',5-difluoro-biphenyl-2-yl)-3-trifluoromethyl-1 -methyl-1H-pyrazole-4-carboxamide, N-(3',4'- dichloro-5-fluoro-biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',5-difluoro-4'-methyl-biphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',5-difluoro-4'-methyl-biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(cis-2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(trans-2-bicyclopropyl-2-yl-phenyl)-3-difluoro-methyl-1-methyl-1 H-pyrazole-4-carboxamide, fluopyram, N-(3-ethyl-3,5-5- trimethyl-cyclohexyl)-3-formylamino-2-hydroxy-benzamide, oxytetracyclin, silthiofam, N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxamide, 2-iodo-N-phenyl-benzamide, N-(2-bicyclo-propyl-2-yl-phenyl)-3-difluormethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1,3-dimethyl-pyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3- fluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'- trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4- ylcarboxamide,N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-

methylpyrazol-4- ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5-fluoro-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2- yl)-5-chloro-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N- (3', 4', 5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)- 5-fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3- trifluoromethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-ylcarboxamide, N-(2',4',5'- trifluorobiphenyl-2-yl)-5-chloro-1 ,3-dimethylpyrazol-4-ylcarboxamide, N- (2',4',5'-trifluorobiphenyl-2-yl)-3-fluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4-ylcarboxamide,N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5- fluoro-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N- (2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3- trifluoromethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)- 5-fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(2',4',5'- trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(3',4'-dichloro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-3- fluorobiphenyl-2-yl)-1 -methyl-3-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-S-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3'-chloro-4'- fluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1 H-pyrazole-4-carboxamide, N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1 H- pyrazole-4-carboxamide, N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1- methyl-S-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-4- fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H- pyrazole-4-carboxamide, N-(3'-chloro-4'-fluoro-4-fluorobiphenyl-2-yl)-1-methyl-S-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5- fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-difluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H- pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1-methyl-S-difluoromethyl-1H-

pyrazole-4-carboxamide, N-(3',4'-difluoro-5- fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1 H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazole-4-carboxamide, N-(3'-chloro-4'-fluoro-5-fluorobiphenyl-2-yl)-1-methyl-3- difluoromethyl-1H-pyrazole-4-carboxamide, N-(4'-fluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(4'-fluoro- 5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide,N-(4'-chloro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H- pyrazole-4-carboxamide, N-(4'-methyl-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(4'-fluoro-5- fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazole-4-carboxamide, N-(4'- chloro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazole-4-carboxamide, N-(4'-methyl-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazole-4-carboxamide, N-(4'-fluoro-6-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H- pyrazole-4-carboxamide, N-(4'-chloro-6-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-[2-(1,1,2,3,3,3- hexafluoropropoxy)-phenyl]-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-[4'-(trifluoromethylthio)-biphenyl-2-yl]-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide and N-[4'-(trifluoromethylthio)-biphenyl-2-yl]-1-methyl-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxamide; B4) heterocyclic compounds selected from the group consisting of fluazinam, pyrifenox, bupirimate, cyprodinil, fenarimol, ferimzone, mepanipyrim, nuarimol, pyrimethanil, triforine, fenpiclonil, fludioxonil, aldimorph, dodemorph, fenpropimorph, tridemorph, fenpropidin, iprodione, procymidone, vinclozolin, famoxadone, fenamidone, octhilinone, proben- azole, 5-chloro-7-(4-methyl-piperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, anilazine, diclomezine, pyroquilon, proquinazid, tricyclazole, 2-butoxy-6-iodo-3-propylchromen-4-one, acibenzolar-S-methyl, captafol, captan, dazomet, folpet, fenoxanil, quinoxyfen, N,N-dimethyl-3-(3-bromo-6-fluoro-2-methylindole-1-sulfonyl)- [1,2,4]triazole-1-sulfonamide, 5-ethyl-6-octyl-[1,2,4]triazolo[1,5-a]pyrimidin-2,7-diamine, 2,3,5,6-tetrachloro-4-methanesulfonyl-pyridine, 3,4,5-trichloro-pyridine-2,6-di-carbonitrile, N-(1-(5-bromo-3-chloro-pyridin-2-yl)-ethyl)-2,4-dichloro-nicotinamide, N-((5-bromo-3-chloro pyridin-2-yl)-methyl)-2,4-dichloro-nicotinamide, diflumetorim, nitrapyrin, dodemorphacetate, fluoroimid, blasticidin-S, chinomethionat, debacarb, difenzoquat, difenzoquat-methylsulphate, oxolinic acid and piperalin; B5) carbamates selected from the group consisting of mancozeb, maneb, metam, methasulphocarb, metiram, ferbam, propineb, thiram, zineb, ziram, diethofencarb, iprovalicarb, benthiavalicarb, propamocarb, propamocarb hydrochlorid, 4-fluorophenyl N-(1-(1-(4-cyanophenyl)- ethanesulfonyl)but-2-yl)carbamate, methyl 3-(4-chloro-phenyl)-3-(2-

isopropoxycarbonylamino-3-methyl-butyrylamino)propanoate; or B6) other fungicides selected from the group consisting of guanidine, dodine, dodine free base, iminoctadine, guazatine, antibiotics: kasugamycin, streptomycin, polyoxin, validamycin A, nitrophenyl derivatives: binapacryl, dinocap, dinobuton, sulfur-containing heterocyclyl compounds: dithianon, isoprothiolane, organometallic compounds: fentin salts, organophosphorus compounds: edifenphos, iprobenfos, fosetyl, fosetyl-aluminum, phosphorous acid and its salts, pyrazophos, tolclofos- methyl, organochlorine compounds: dichlofluanid, flusulfamide, hexachloro- benzene, phthalide, pencycuron, quintozene, thiophanate-methyl, tolylfluanid, others: cyflufenamid, cymoxanil, dimethirimol, ethirimol, furalaxyl, metrafenone and spiroxamine, guazatine-acetate, iminoctadine-triacetate, iminoctadine-tris(albesilate), kasugamycin hydrochloride hydrate, dichlorophen, pentachlorophenol and its salts, N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-methyl-benzenesulfonamide, dicloran, nitrothal-isopropyl, tecnazen, biphenyl, bronopol, diphenylamine, mildiomycin, oxincopper, prohexadione calcium, N- (cyclopropylmethoxyimino-(6-difluoromethoxy-2,3-difluoro-phenyl)- methyl)-2-phenyl acetamide, N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(4-(4-fluoro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(2-methyl-5-trifluormethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methylformamidine and N'-(5-difluormethyl-2-methyl- 4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine.

Herbicides: C1) acetyl-CoA carboxylase inhibitors (ACC), for example cyclohexenone oxime ethers, such as alloxydim, clethodim, cloproxydim, cycloxydim, sethoxydim, tralkoxydim, butroxydim, clefoxydim or tepraloxydim; phenoxyphenoxypropionic esters, such as clodinafop-propargyl, cyhalofop-butyl, diclofop-methyl, fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenthiapropethyl, fluazifop-butyl, fluazifop-P-butyl, haloxyfop-ethoxyethyl, haloxyfop-methyl, haloxyfop-P-methyl, isoxapyrifop, propaquizafop, quizalofop-ethyl, quizalofop-P-ethyl or quizalofop-tefuryl; or arylaminopropionic acids, such as flamprop-methyl or flamprop-isopropyl; C2 acetolactate synthase inhibitors (ALS), for example imidazolinones, such as imazapyr, imazaquin, imazamethabenz-methyl (imazame), imazamox, imazapic or imazethapyr; pyrimidyl ethers, such as pyrithiobac-acid, pyrithiobac-sodium, bispyribac-sodium. KIH-6127 or pyribenzoxym; sulfonamides, such as florasulam, flumetsulam or metosulam; or sulfonylureas, such as amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron, flazasulfuron, halosulfuron-methyl, imazosulfuron, metsulfuron-methyl, nicosulfuron,

primisulfuron-methyl, prosulfuron, pyrazosulfuron-ethyl, rimsulfuron, sulfometuron-methyl, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, triflusulfuron-methyl, tritosulfuron, sulfosulfuron, foramsulfuron or iodosulfuron; C3) amides, for example allidochlor (CDAA), benzoylprop-ethyl, bromobutide, chlorthiamid. diphenamid, etobenzanid, fluthiamide, fosamin or monalide; C4) auxin herbicides, for example pyridinecarboxylic acids, such as clopyralid or picloram; or 2,4-D or benazolin; C5) auxin transport inhibitors, for example naptalame or diflufenzopyr; C6) carotenoid biosynthesis inhibitors, for example benzofenap, clomazone, diflufenican, fluorochloridone, fluridone, pyrazolynate, pyrazoxyfen, isoxaflutole, isoxachlortole, mesotrione, sulcotrione (chlormesulone), ketospiradox, flurtamone, norflurazon or amitrol; C7) enolpyruvylshikimate-3-phosphate synthase inhibitors (EPSPS), for example glyphosate or sulfosate; C8) glutamine synthetase inhibitors, for example bilanafos or glufosinate-ammonium; C9) lipid biosynthesis inhibitors, for example anilides, such as anilofos or mefenacet; chloroacetanilides, such as dimethenamid, S-dimethenamid, acetochlor, alachlor, butachlor, butenachlor, diethatyl-ethyl, dimethachlor, metazachlor, metolachlor, S-metolachlor, pretilachlor, propachlor, prynachlor, terbuchlor, thenylchlor or xylachlor; thioureas, such as butylate, cycloate, di-allate, dimepiperate, EPTC. esprocarb, molinate, pebulate, prosulfocarb, thiobencarb (benthiocarb), tri-allate or vemolate; or benfuresate or perfluidone; C10) mitosis inhibitors, for example carbamates, such as asulam, carbetamid, chlorpropham, orbencarb, propyzamid, propham or tiocarbazil; dinitroanilines, such as benefin, butralin, dinitramin, ethalfluralin, fluchloralin, oryzalin, pendimethalin, prodiamine or trifluralin; pyridines, such as dithiopyr or thiazopyr; or butamifos, chlorthal-dimethyl (DCPA) or maleic hydrazide; C11) protoporphyrinogen IX oxidase inhibitors, for example diphenyl ethers, such as acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlomitrofen (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen, nitrofluorfen or oxyfluorfen; oxadiazoles, such as oxadiargyl or oxadiazon; cyclic imides, such as azafenidin, butafenacil, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone or thidiazimin; or pyrazoles, such as ET-751, JV 485 or nipyraclofen; C12) photosynthesis inhibitors, for example propanil, pyridate or pyridafol; benzothiadiazinones, such as bentazone; dinitrophenols, for example bromofenoxim, dinoseb, dinoseb-acetate, dinoterb or DNOC; dipyridylenes, such as cyperquat-chloride, difenzoquat-methylsulfate, diquat or paraquat-dichloride; ureas, such as chlorbromuron, chlorotoluron, difenoxuron, dimefuron, diuron, ethidimuron, fenuron, fluometuron, isoproturon, isouron, linuron, methabenzthiazuron, methazole, metobenzuron, metoxuron, monolinuron, neburon, siduron

or tebuthiuron; phenols, such as bromoxynil or ioxynil; chloridazon; triazines, such as ametryn, atrazine, cyanazine, desmein, dimethamethryn, hexazinone, prometon, prometryn, propazine, simazine, simetryn, terbumeton, terbutryn, terbutylazine or trietazine; triazinones, such as metamitron; uracils, such as bromacil, lenacil or terbacil; or biscarbamates, such as desmedipham or phenmedipham; C13) synergists, for example oxiranes, such as tridiphane; C14) CIS cell wall synthesis inhibitors, for example isoxaben or dichlobenil; C16) various other herbicides, for example dichloropropionic acids, such as dalapon; dihydrobenzofurans, such as ethofumesate; phenylacetic acids, such as chlorfenac (fenac); or aziprotryn, barban, bensulide, benzthiazuron, benzofluor, buminafos, buthidazole, buturon, cafenstrole, chlorbufam, chlorfenprop-methyl, chloroxuron, cinmethylin, cumyluron, cycluron, cyprazine, cyprazole, dibenzyluron, dipropetryn, dymron, eglinazin-ethyl, endothall, ethiozin, flucabazone, fluorbentranil, flupoxam, isocarbamid, isopropalin, karbutilate, mefluidide, monuron, napropamide, napropanilide, nitralin, oxaciclomefone, phenisopham, piperophos, procyazine, profluralin, pyributicarb, secbumeton, sulfallate (CDEC), terbucarb, triaziflam, triazofenamid or trimeturon; or their environmentally compatible salts.

Plant Growth Regulators: D1) Antiauxins, such as clofibric acid, 2,3,5-tri-iodobenzoic acid; D2) Auxins such as 4-CPA, 2,4-D, 2,4-DB, 2,4-DEP, dichlorprop, fenoprop, IAA ,IBA, naphthaleneacetamide, α-naphthaleneacetic acids, 1-naphthol, naphthoxyacetic acids, potassium naphthenate, sodium naphthenate, 2,4,5-T; D3) cytokinins, such as 2iP, benzyladenine, 4-hydroxyphenethyl alcohol, kinetin, zeatin; D4) defoliants, such as calcium cyanamide, dimethipin, endothal, ethephon, merphos, metoxuron, pentachlorophenol, thidiazuron, tribufos; D5) ethylene inhibitors, such as aviglycine, 1-methylcyclopropene; D6) ethylene releasers, such as ACC, etacelasil,ethephon, glyoxime; D7) gametocides, such as fenridazon, maleic hydrazide; D8) gibberellins, such as gibberellins, gibberellic acid; D9) growth inhibitors, such as abscisic acid, ancymidol, butralin, carbaryl, chlorphonium, chlorpropham, dikegulac, flumetralin, fluoridamid, fosamine, glyphosine, isopyrimol, jasmonic acid, maleic hydrazide, mepiquat, piproctanyl, prohydrojasmon, propham, tiaojiean, 2,3,5-tri-iodobenzoic acid; D10) morphactins, such as chlorfluren, chlorflurenol, dichlorflurenol, flurenol; D11) growth retardants, such as chlormequat, daminozide, flurprimidol, mefluidide, paclobutrazol, tetcyclacis, uniconazole; D12) growth stimulators, such as brassinolide, brassinolide-ethyl, DCPTA, forchlorfenuron, hymexazol, prosuler, triacontanol; D13) unclassified plant growth regulators, such as bachmedesh, benzofluor, buminafos, carvone, choline chloride, ciobutide, clofencet, cyanamide, cyclanilide, cycloheximide, cyprosulfamide, epocholeone, ethychlozate, ethylene,

fuphenthiourea, furalane, heptopargil, holosulf, inabenfide, karetazan, lead arsenate, methasulfocarb, prohexadione, pydanon, sintofen, triapenthenol, trinexapac.

The compositions of the present disclosure can also include a preservative. Suitable preservatives include but are not limited to C_{12} to C_{15} alkyl benzoates, alkyl p-hydroxybenzoates, aloe vera extract, ascorbic acid, benzalkonium chloride, benzoic acid, benzoic acid esters of C_9 to C_{15} alcohols, butylated hydroxytoluene, butylated hydroxyanisole, tert-butylhydroquinone, castor oil, cetyl alcohols, chlorocresol, citric acid, cocoa butter, coconut oil, diazolidinyl urea, diisopropyl adipate, dimethyl polysiloxane, DMDM hydantoin, ethanol, ethylenediaminetetraacetic acid, fatty acids, fatty alcohols, hexadecyl alcohol, hydroxybenzoate esters, iodopropynyl butylcarbamate, isononyl iso-nonanoate, jojoba oil, lanolin oil, mineral oil, oleic acid, olive oil, parabens, polyethers, polyoxypropylene butyl ether, polyoxypropylene cetyl ether, potassium sorbate, propyl gallate, silicone oils, sodium propionate, sodium benzoate, sodium bisulfite, sorbic acid, stearic fatty acid, sulfur dioxide, vitamin E, vitamin E acetate and derivatives, esters, salts and mixtures thereof. Preferred preservatives include sodium o-phenylphenate, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and 1,2-benisothiazolin-3-one.

As used in this application and unless otherwise indicated the term "herbicide" refers to a compositional mixture that is produced, sold, or used in a field in order to kill or otherwise inhibit unwanted plants such as, but not limited to, deleterious or annoying weeds, broadleaf plants, grasses, and sedges; and can be used for crop protection, edifice protection or turf protection. The term "herbicide" includes the end-use herbicidal product. This composition can be a pure compound, a solution of chemical compounds, a mixture of chemical compounds, an emulsion, a suspension, a solid-liquid mixture, or a liquid- liquid mixture. The term "herbicide" also refers to the product that passes through the commercial channels from the manufacturer to the ultimate end user who can either apply the herbicide to the affected field as sold, or mix it with other excipients.

The term "plant" means and includes any plant which grows where not wanted.

The term "herbicidally effective amount" means an amount necessary to produce an observable herbicidal effect on unwanted plant growth, including one or more of the effects of necrosis, death, growth inhibition, reproduction inhibition, inhibition of proliferation, and removal, destruction, or otherwise diminishing the occurrence and activity of unwanted plants.

The term "herbicidally active ingredient" means the active ingredient in the herbicide that causes the herbicide to prevent, destroy, repel or mitigate any weed. Other ingredients of

the herbicide that are not herbicidally active ingredients are excipients that aid in forming, storing, or delivering herbicidally active ingredient to the target. Examples of excipients in the present embodiment include, without limitation, an organic liquid in which herbicidally active ingredient is dissolved, a polyurea shell, a water-soluble polymer, and one or more salts.

The definition of the term "herbicidal composition" refers to a herbicide, and in addition, to any composition that comprises a herbicidally active ingredient. This composition can be a solution or a mixture. Further, the definition of the term "herbicidal composition" also refers to a product intended for use in manufacruting, or any product intended for formulation or repackaging into other agricultural products.

One aspect of the invention is directed to a method for the selective control of a plant in the *Brassicaceae family* in a cereal crop, comprising applying to the *Brassicaceae* plant a herbicidally effective amount of a composition comprising (a) a photosystem II inhibitor, and (b) a protoporphyrinogen oxidase inhibitor. In one embodiment of the method, the composition is applied at a rate of about 10 g ai/acre to about 500g ai/acre. In another embodiment the composition is applied at a rate of about 50 g ai/acre to about 120 g ai/acre. In one embodiment of the method, the cereal crop is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio. In another embodiment of the method, the composition comprises (a) a photosystem II inhibitor and (b) a protoporphyrinogen oxidase inhibitor in a formulation selected from the group consisting of water dispersible granular formulations, emulsion concentrates, suspension concentrates, suspo-emulsions, capsule suspensions, emulsifiable granules, water in oil emulsions, oil in water emulsions, micro-emulsions, oil dispersions, oil miscible flowables, oil miscible liquids, soluble concentrates, ultra-low volume suspensions, ultra-low volume liquids, dispersible concentrates, and wettable powders. In a preferred embodiment of the method the photosystem II inhibitor is selected from the group consisting of ametryn, atrazine, cyanazine, hexazinone, metribuzin, and simazine. In a more preferred embodiment the photosystem II inhibitor is metribuzin. In one embodiment of the method, the protoporphyrinogen oxidase inhibitor is selected from the group consisting of acifluorfen-sodium, bifenox, chlomethoxyfen, chlornitrofen, ethoxyfen-ethyl, fluorodifen, fluoroglycofen-ethyl, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen, oxyfluorfen, cinidon-ethyl, flumiclorac-pentyl, flumioxazine, profluazol, pyrazogyl, oxadiargyl, oxadiazon, pentoxazone, fluazolate, pyraflufen-ethyl, benzfendizone,

butafenacil, fluthiacet-methyl, thidiazimin, azafenidin, carfentrazone-ethyl, sulfentrazone, and flufenpyr-ethyl. Preferably the protoporphyrinogen oxidase inhibitor is carfentrazone-ethyl. In one embodiment of the method the plant in the *Brassicaceae* family comprises *Raphanus raphanistrum*. Preferably the plant is *Raphanus raphanistrum*.

Another aspect of the invention is directed to a method for the selective control of the plant *Raphanus raphanistrum* in a cereal crop, comprising applying to *Raphanus raphanistrum* a herbicidally effective amount of a composition comprising (a) metribuzin, and (b) carfentrazone-ethyl. In one embodiment of the method, the composition is applied at a rate of about 10 g ai/acre to about 500g ai/acre. In another embodiment the composition is applied at a rate of about 50 g ai/acre to about 120 g ai/acre. In one embodiment of the method the cereal crop is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio.

Another aspect of the invention is directed to a composition for selectively controlling the plant *Raphanus raphanistrum* in a cereal crop, the composition comprising carfentrazone-ethyl and a photosystem II inhibitor in a ratio of about 1:4 to about 1:20 by weight, which selectively controls the plant *Raphanus raphanistrum* in a cereal crop. In one embodiment of the composition the ratio is about 1:4.2. In one embodiment of the composition the photosystem II inhibitor is selected from the group consisting of ametryn, atrazine, cyanazine, hexazinone, metribuzin, and simazine. Preferably the photosystem II inhibitor is metribuzin. In one embodiment of the composition, the cereal crop to which it is applied is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio. In one embodiment, the composition is in the form of a suspension concentrate. In one embodiment of the composition, the ratio of carfentrazone-ethyl:photosystem II inhibitor shows synergism in the control of *Raphanus raphanistrum.*

The following examples serve only to illustrate the invention and should not be interpreted as limiting the scope of the invention in any way, since further modifications encompassed by the disclosed invention will be apparent to those skilled in the art. All such modifications are deemed to be within the scope of the invention as defined in the present specification and claims.

EXAMPLES

EXAMPLE 1. Preparation of Water Dispersible Granules Containing Carfentrazone-ethyl and Metribuzin

Step A: 2.766 kilograms of warm (80°C) HISIL® silica (PPG Industries) was charged to a preheated (85-90°C) Littleford mixer. Warm carfentrazone-ethyl (80°C, 4.037 kilograms, 91.0% pure) was charged to a pressure spray canister. The mill and plow was started on the mixer and the warm carfentrazone-ethyl was sprayed onto the silica. The mixer continued mixing for about 15 minutes after all the carfentrazone-ethyl was applied. The mixer was stopped and the contents discharged into a stainless steel can and placed into an 80°C oven for about 16 hours. The can was allowed to cool to room temperature. Analysis of a sample of this powder by HPLC indicated an assay of 53.2% carfentrazone by weight.

Step B: Into a ribbon blender was added 5.581 kilograms of technical metribuzin (95.2% pure), 393.0 grams of a kraft lignosulfonate (POLYFON® O dispersant, MeadWestvaco Corporation), 131.2 grams of N-methyl oleyl taurate (GEROPON T-77, Rhodia-Novecare), 380.0 grams of an anionic sodium polycarboxylate (GEROPON T-36, Rhodia-Novecare), 972.6 grams of ammonium sulfate and 972.6 grams of continental clay. This was mixed for 10 minutes, discharged to a hammermill affixed with a 0.13 screen. The powder collected was determined to have an average particle size, D90 of less than 15 microns. 4.522 kilograms of this powder and 920.8 grams of the carfentrazone-ethyl powder were charged to a kneading machine and 690.0 grams of water was sprayed onto the mixture, forming dough-like material. The dough was extruded through a 1.0 millimeter die into metal trays. The trays were placed into a 55°C oven until a loss on drying at 60°C was less than 0.8%. Analysis of the water dispersible granules (WDG) by HPLC indicated 9.2% by weight carfentrazone-ethyl and 38.4% by weight metribuzin (a wt% to wt% ratio of 1:4.2).

EXAMPLE 2. Preparation of Water Dispersible Granules Containing Carfentrazone-ethyl and Metribuzin

Into a ribbon blender was added 10.478 kilograms of technical metribuzin (95.2% pure), 1.633 kilograms of a kraft lignosulfonate (POLYFON® O dispersant, MeadWestvaco Corporation), 544.3 grams of a linear alkylbenzene sulfonate (STEPWET® DF-90 surfactant, Stepan Company), 1.633 kilograms of an anionic sodium polycarboxylate (Geropon T-36, Rhodia-Novecare), 272.2 grams of a powder defoamer (AGNIQUE® SOAP L, BASF), 13.6 grams of citric acid, 4.053 kilograms of ammonium sulfate and 4.053 kilograms of continental clay. This was mixed for 10 minutes then discharged to a hammermill affixed

with a 0.13 screen. The powder collected was determined to have an average particle size, D90 of less than 20 microns. 18.9 kilograms of this powder and 3.780 kilograms of the carfentrazone-ethyl powder prepared as in Example 1, Step A, were charged to a kneading machine and 3.692 kilograms of water was sprayed onto the mixture, forming dough-like material. The dough was extruded through a 0.8 millimeter die into metal trays. The trays were placed into a 55°C oven until a loss on drying at 60°C was less than 0.8%. Analysis of the granules by HPLC indicated 9.04% by weight carfentrazone-ethyl and 37.6% by weight metribuzin (a wt% to wt% ratio of 1:4.2).

Additional formulations were prepared in the manner of Example 2 and are summarized in Table 1 below. The carfentrazone-ethyl powder was prepared as in Example 1, Step A. The ingredient amounts are presented in a percent by weight of the total formulation.

Table 1. Carfentrazone-ethyl and Metribuzin WDG Formulations (% by weight)

Ingredient	Ex 2-2	Ex 2-3	Ex 2-4	Ex 2-5	Ex 2-6	Ex 2-7	Ex 2-8	Ex 2-9
Ex 1, Step A	16.42	16.42	16.42	16.42	16.42	16.42	16.42	16.42
Metribuzin	39.02	39.02	39.02	39.02	39.02	39.02	39.02	39.02
Antifoam DF-90	2	2	2	2	2	2	2	2
POLYFON O	6	4	4	4	8	6	4	6
MORWET D-425*	4	5	0	0	0	0	0	0
TERSPERSE 2425**	0	0	4	0	2	2	2	0
GEOPRON T-36	0	0	0	6	0	0	0	6
Cont.clay	16.28	16.78	17.28	16.28	17.28	16.28	18.28	15.28
Ammonium Sulfate	16.28	16.78	17.28	16.28	17.28	16.28	18.28	15.28

* MORWET® D-425 Powder is a sodium salt of naphthalene sulfonate condensate available from AKZO NOBEL

** TERSPERSE® 2425 is an alkyl naphthalene sulfonate formaldehyde condensate available from Huntsman Corporation.

EXAMPLE 3. Control of Wild Radish Using Carfentrazone-ethyl and Metribuzin WDG Formulations

Test solutions of Example 1 formulation were made by diluting with water to achieve the desired test rate. Treatments were applied to test plots (2 m x 10 m, located in Kojonup, Western Australia) as a randomized complete block design with four replicates. Each treatment was applied using a gas operated sprayer with hand boom incorporating AgroTop

AirMix Flat Fan Nozzles AM11001 at an application speed of 1.3 m/sec and a pressure of 200kPa, applied in a total volume of 80 L/ha. The treatments were applied to a barley crop (Baudin variety) at the three leaves unfolded growth stage to main shoot and 2 tiller growth stage (Zadocks scale13 – 22). The infestation of wild radish (*Raphanus raphanistrum*) was 10 plants/m^2. The weed population over the trial period remained consistent with no significant natural mortality or new germinations observed in the control plots. Test plots in which carfentrazone-ethyl (AFFINITY FORCE® HERBICIDE (AFH), an oil in water emulsion containing 240g/L AI marketed by FMC Australasia Pty Limited) and metribuzin (STACATO® 750WG HERBICIDE (S 750), a water dispersible granule containing 750 g/Kg AI marketed by Sipcam Pacific Australia Pty Limited) were included in the trial. Assessments of weed control and crop phytotoxicity were made at 8, 18, 28, and 42 days after treatment (DAT) and the average results are summarized in Table 2 below.

Table 2. Average Wild Radish Control and Crop Toxicity Of Carfentrazone-ethyl, Metriuzin and WDG Formulation Thereof

Treatment	Rate (g/ha), or (g/Carfentrazone/ha; g metribuzin/ha)	% Average Weed Control or Crop Toxicity							
		8 DAT		18 DAT		28 DAT		42 DAT	
		Weed Control	Crop Toxicity	Weed Control	Crop Toxicity	Weed Control	Crop Toxicity	Weed Control	Crop Toxicity
Untreated	--	0	0	0	0	0	0	0	0
AFH	18	22.5	5.0	62.5	3.8	22.5	0	20.0	0
S 750	75	10.0	0	45.0	0	15.0	0	12.5	0
Ex 1	12.2; 51	27.5	5.0	83.8	0	90.8	0	94.5	0
Ex 1*	18.4; 76.8	30.0	5.0	90.8	2.5	95.0	0	96.5	0
Ex 1	24.5; 102.5	32.5	6.3	90.0	2.5	99.0	0	98.5	0
Ex 1	36.8; 190.4	45.0	6.3	93.8	5.0	99.5	0	99.5	0

The data in Table 2 indicates that the formulation of Example 1 is far superior individual treatments of carfentrazone-ethyl or metribuzin in controlling wild radish in cereals such as barley. In fact the herbicidal control data indicates a surprising synergistic affect when applying the Colby equation for "Calculating synergistic and antagonistic responses of herbicide combinations" (Weeds, vol:15; no1, 20-22, 1967), E=X+Y-[(X)(Y)/100]. Using the method of Colby, the presence of a synergistic interaction between two active ingredients is established by first calculating the expected activity, 'E', of the mixture based on activities of the two components applied alone. In the equation above, 'X'

is the herbicidal activity in percentage control of carfentrazone-ethyl applied alone at rate 'x'. The 'Y' term is the herbicidal activity of metribuzin applied alone at rate 'y'. The equation calculates 'E', the herbicidal activity of the mixture of 'X' at rate 'x' with 'Y' at rate 'y'. If 'E' is lower than the observed activity, synergy is present. If the herbicidal effects are strictly additive, and no interaction has occurred, 'E' will be equal to or higher than the observed activity.

When applying the Colby Equation to the data shown for Ex 1* and that of AFFINITY FORCE® HERBICIDE and STACATO® 750WG HERBICIDE, synergy was observed for 18, 28 and 42 DAT. This data is presented in Table 2A below.

Table 2A. Synergistic Effect of WDG Formulation Containing Carfentrazone-ethyl and Metribuzin

Treatment	Rate (g/ha), or (g/Carfentrazone/ha; g metribuzin/ha)	% Average Weed Control vs Expected Control							
		8 DAT		18 DAT		28 DAT		42 DAT	
		Weed Control	Expected Control	Weed Control	Expected Control	Weed Control	Expected Control	Weed Control	Expected Control
AFH	18	22.5		62.5		22.5		20.0	
S 750	75	10.0		45.0		15.0		12.5	
Ex 1*	18.4; 76.8	30.0	30	90.8	79	95.0	34	96.5	30

As can be seen from the data in Table 2A, the formulation of Example 1* surprisingly exhibits 66% more control of wild radish than would be expected at 42 DAT.

While this invention has been described with an emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations in the preferred compositions and methods can be used and that it is intended that the invention can be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the claims that follow.

CLAIMS

What is claimed is:

1. A method for the selective control of a plant in the *Brassicaceae family* in a cereal crop, comprising applying to said *Brassicaceae* plant a herbicidally effective amount of a composition comprising (a) a photosystem II inhibitor, and (b) a protoporphyrinogen oxidase inhibitor.

2. The method of claim 1, wherein the composition is applied at a rate of about 10 g ai/acre to about 500g ai/acre.

3. The method of claim 2, wherein the composition is applied at a rate of about 50 g ai/acre to about 120 g ai/acre.

4. The method of claim 1, wherein the cereal crop is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio.

5. The method of claim 1, wherein the composition comprises (a) a photosystem II inhibitor and (b) a protoporphyrinogen oxidase inhibitor in a formulation selected from the group consisting of water dispersible granular formulations, emulsion concentrates, suspension concentrates, suspo-emulsions, capsule suspensions, emulsifiable granules, water in oil emulsions, oil in water emulsions, micro-emulsions, oil dispersions, oil miscible flowables, oil miscible liquids, soluble concentrates, ultra-low volume suspensions, ultra-low volume liquids, dispersible concentrates, and wettable powders.

6. The method of claim 1, wherein the photosystem II inhibitor is selected from the group consisting of ametryn, atrazine, cyanazine, hexazinone, metribuzin, and simazine.

7. The method of claim 6, wherein the photosystem II inhibitor is metribuzin.

8. The method of claim 1, wherein the protoporphyrinogen oxidase inhibitor is selected from the group consisting of acifluorfen-sodium, bifenox, chlomethoxyfen, chlornitrofen, ethoxyfen-ethyl, fluorodifen, fluoroglycofen-ethyl, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen, oxyfluorfen, cinidon-ethyl, flumiclorac-pentyl, flumioxazine, profluazol, pyrazogyl, oxadiargyl, oxadiazon, pentoxazone, fluazolate, pyraflufen-ethyl, benzfendizone, butafenacil, fluthiacet-methyl, thidiazimin, azafenidin, carfentrazone-ethyl, sulfentrazone, and flufenpyr-ethyl.

9. The method of claim 8, wherein the protoporphyrinogen oxidase inhibitor is carfentrazone-ethyl.

10. The method of claim 1, wherein the plant in the *Brassicaceae* family comprises *Raphanus raphanistrum*.

11. A method for the selective control of the plant *Raphanus raphanistrum* in a cereal crop, comprising applying to said *Raphanus raphanistrum* a herbicidally effective amount of a composition comprising (a) metribuzin, and (b) carfentrazone-ethyl.

12. The method of claim 11, wherein the composition is applied at a rate of about 10 g ai/acre to about 500g ai/acre.

13. The method of claim 12, wherein the composition is applied at a rate of about 50 g ai/acre to about 120 g ai/acre.

14. The method of claim 11, wherein the cereal crop is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio.

15. A composition for selectively controlling the plant *Raphanus raphanistrum* in a cereal crop, said composition comprising carfentrazone-ethyl and a photosystem II inhibitor in a ratio of about 1:4 to about 1:20 by weight, which selectively controls the plant *Raphanus raphanistrum* in a cereal crop.

16. The composition of claim 15, wherein the photosystem II inhibitor is selected from the group consisting of ametryn, atrazine, cyanazine, hexazinone, metribuzin, and simazine.

17. The composition of claim 16, wherein the photosystem II inhibitor is metribuzin.

18. The composition of claim 17, wherein the ratio is about 1:4.2.

19. The composition of claim 15, wherein the cereal crop is selected from the group consisting of wheat, barley, rice, corn, sorghum, millet, oats, rye, triticale, and fonio.

20. The composition of claim 15, wherein said composition is in the form of a suspension concentrate.

21. The composition of claim 15, wherein said ratio of carfentrazone-ethyl:photosystem II inhibitor shows synergism in the control of *Raphanus raphanistrum.*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/22740

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A01N 43/707, 43/40, 43/64 (2015.01)
CPC - A01N 43/707, 43/40, 43/64
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) Classification(s): A01N 43/707, 43/40, 43/64, 25/02; A01P 13/02 (2015.01)
CPC Classification(s): A01N 43/707, 43/40, 43/64, 25/02

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)
PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google Scholar; Google; ProQuest
brassicaceae, raphanus raphanistrum, photosystem II inhibitor, ametryn, atrazine, cyanazine, hexazinone, metribuzin, simazine, protoporphyrinogen oxidase inhibitor, acifluorfen-sodium, bifenox, chlomethoxyfen, chlomitrofen, ethoxyfen-ethyl, fluorodifen

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7939721 B2 (ARNEVIK, CL et al.) 10 May 2011; claims 1, 20, 23, 32	1-21
A	WO 2009/029518 A2 (DOW AGROSCIENCES LLC) 5 March 2009; page 11, lines 12-13; page 16, lines 1-2; page 61, lines 16-17, lines 17-18	1-21
A	US 2014/0031210 A1 (YERKES, CN et al.); 30 January 2014; paragraph [0050]	1-21
A	US 6,723,681 B2 (HACKER, E et al.) 20 April 2004; claim 1	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* 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)
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"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
27 May 2015 (27.05.2015)	29 JUN 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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