



(51) International Patent Classification:
B01J 27/14 (2006.01)

(21) International Application Number:
PCT/US2012/043526

(22) International Filing Date:
21 June 2012 (21.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/500,784 24 June 2011 (24.06.2011) US

(71) Applicant (for all designated States except US): **DOW AGROSCIENCES LLC** [US/US]; 9330 Zionsville Road, Indianapolis, IN 46268 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MANN, Richard, K.** [US/US]; 1828 South 550 East, Franklin, IN 46131 (US). **NGUYEN, Lap** [VN/VN]; 385/22 Nguyen Dinh Chieu Street, District 3, Hcm City (VN). **SAMANWONG, Som-sak** [TH/TH]; 89/40 Vista Park-Changwattana, Moo 3, Li-enmuang Pakret Rd, Bangtalard, Pakret, Nonthaburi, 11120 (TH).

(74) Agent: **CHANG, Robert**; Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, Indiana 46268 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

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

(54) Title: SYNERGISTIC HERBICIDAL COMPOSITION CONTAINING PENOXSULAM AND PENDIMETHALIN

(57) Abstract: A synergistic herbicidal composition containing (a) penoxsulam and (b) pendimethalin provides improved pre-emergence to early post-emergence herbicidal weed control of undesirable vegetation in multiple crops, including rice, cereal and grain crops, turf, IVM, sugar cane and tree and vine orchards. The active ingredient ratio (weight-to-weight) of pendimethalin to penoxsulam at which the herbicidal effect is synergistic lies within the range of between about 5:1 and 320:1, and in certain embodiments, a ratio of about 55:1. The rate at which the synergistic composition is applied will depend upon the particular type of weed to be controlled, the degree of control required, and the timing and method of application. The composition of the invention can be applied at an application rate of between about 160 grams active ingredient per hectare 30 (gai/ha) and about 1850 gai/ha based on the total amount of active ingredients in the composition.



SYNERGISTIC HERBICIDAL COMPOSITION
CONTAINING PENOXSULAM AND PENDIMETHALIN

Cross Reference to Related Applications

5 This Application claims the benefit of U.S. provisional application 61/500,784 filed on June 24, 2011. The entire content of this provisional application is hereby incorporated by reference into this Application.

Field

10 This invention concerns a synergistic herbicidal composition containing (a) penoxsulam and (b) pendimethalin for controlling growth of undesirable vegetation, particularly in multiple crops, including rice, cereal and grain crops, turf, industrial vegetation management (IVM), sugar cane and tree and vine orchards.

Background

15 The protection of crops from weeds and other vegetation which inhibit crop growth is a constantly recurring problem in agriculture. To help combat this problem, researchers in the field of synthetic chemistry have produced an extensive variety of chemicals and chemical formulations effective in the control of such unwanted growth. Chemical herbicides of many types have been disclosed in the literature and a large number are in commercial use.

20 In some cases, herbicidal active ingredients have been shown to be more effective in combination than when applied individually and this is referred to as “synergism.” As described in the *Herbicide Handbook* of the Weed Science Society of America, Ninth Edition, 2007, p. 429, “‘synergism’ [is] an interaction of two or more factors such that the effect when combined is greater than the predicted effect based on the response to each factor applied separately.” The present invention is based on the discovery that pendimethalin and
25 penoxsulam, already known individually for their herbicidal efficacy, display a synergistic effect when applied in combination.

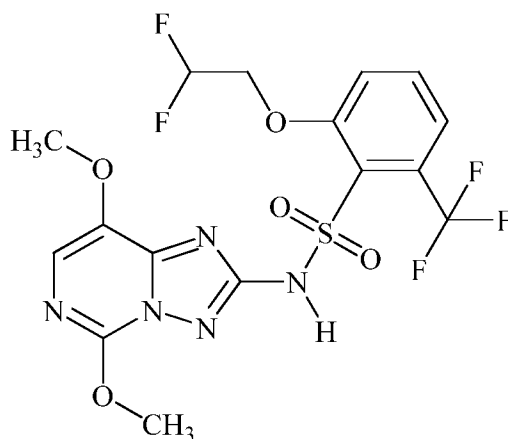
Summary

The present invention concerns a synergistic herbicidal mixture comprising an herbicidally effective amount of (a) penoxsulam and (b) pendimethalin. The compositions may also contain an agriculturally acceptable adjuvant or carrier.

- 5 The present invention also concerns a method of controlling the growth of undesirable vegetation in multiple crops, including rice, cereal and grain crops, turf, IVM, sugar cane and tree and vine orchards, and the use of this synergistic composition.

Detailed Description of the Invention

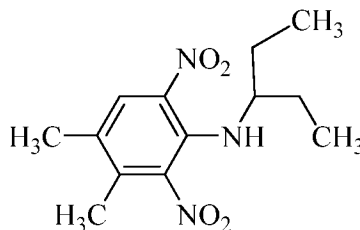
- Penoxsulam is the common name for (2-(2,2-difluoroethoxy)-*N*-(5,8-dimethoxy-
10 [1,2,4]triazolo[1,5-*c*]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide. Its structure is



Its herbicidal activity is described in *The Pesticide Manual*, Fifteenth Edition, 2009.

Penoxsulam controls barnyard grass, as well as many broadleaf and sedge weeds in rice, turf, tree nut and vineyard crops, cereal and grain crops, and IVM.

- 15 Pendimethalin is the common name for *N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine. Its structure is:



Its herbicidal activity is described in *The Pesticide Manual*, Fifteenth Edition, 2009.

Pendimethalin controls most annual grasses and many annual broadleaf weeds in a variety of crops.

The term herbicide is used herein to mean an active ingredient that kills, controls or otherwise adversely modifies the growth of plants. An herbicidally effective or vegetation controlling amount is an amount of active ingredient which causes an adversely modifying effect and includes deviations from natural development, killing, regulation, desiccation, retardation, and the like. The terms plants and vegetation include germinant seeds, emerging seedlings, plants emerging from vegetative propagules, and established vegetation.

Herbicidal activity is exhibited by the compounds of the synergistic mixture when they are applied directly to the plant or to the locus of the plant at any stage of growth or before planting or emergence. The effect observed depends upon the plant species to be controlled, the stage of growth of the plant, 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. These and other factors can be adjusted as is known in the art to promote non-selective or selective herbicidal action.

Generally, it is preferred to apply the composition of the present invention preemergence to early postemergence to relatively immature undesirable vegetation to achieve the maximum control of weeds.

In the composition of this invention, the active ingredient ratio (weight-to-weight, wt:wt) of pendimethalin to penoxsulam at which the herbicidal effect is synergistic lies within the range of between about 5:1 and 320:1, and in certain embodiments, a ratio of about 55:1. In other embodiments, the ratio is in the range of 224:1 to 3:1. In certain embodiments, the ratio is in the range of 55:1 to 17:1.

The rate at which the synergistic composition is applied will depend upon the particular type of weed to be controlled, the degree of control required, and the timing and method of application. In some embodiments, the composition of the invention can be applied at an application rate of between about 160 grams active ingredient per hectare (gai/ha) and about 1850 gai/ha based on the total amount of active ingredients in the composition. In other embodiments, the composition of the invention can be applied at an

application rate of between about 130 grams active ingredient per hectare (gai/ha) and about 2290 gai/ha based on the total amount of active ingredients in the composition. In certain embodiments, an application rate between about 760 gai/ha and about 1800 gai/ha is preferred. In other embodiments, an application rate between about 180 gai/ha and about 1730 gai/ha is preferred. In some embodiments, pendimethalin is applied at a rate between about 150 gai/ha and about 1500 gai/ha, and penoxsulam is applied at a rate between about 10 gai/ha and about 50 gai/ha. In some embodiments, the pendimethalin is applied at a rate between about 500 gai/ha and about 1100 gai/ha, and penoxsulam is applied at a rate between about 10 gai/ha and about 40 gai/ha.

The components of the synergistic mixture of the present invention can be applied either separately or as part of a multipart herbicidal system.

The synergistic mixture of the present invention can be applied in conjunction with one or more other herbicides to control a wider variety of undesirable vegetation. When used in conjunction with other herbicides, the composition can be formulated with the other herbicide or herbicides, tank mixed with the other herbicide or herbicides or applied sequentially with the other herbicide or herbicides. Some of the herbicides that can be employed in conjunction with the synergistic composition of the present invention include: 4-CPA, 4-CPB, 4-CPP, 2,4-D choline salt, esters and amines, 3,4-DA, 2,4-DB, 3,4-DB, 2,4-DEB, 2,4-DEP, 3,4-DP, 2,3,6-TBA, 2,4,5-T, 2,4,5-TB, acetochlor, acifluorfen, aclonifen, acrolein, alachlor, allidochlor, alloxymid, allyl alcohol, alorac, ametrifone, ametryn, amibuzin, amicarbazone, amidosulfuron, aminocyclopyrachlor, aminopyralid, amiprofos-methyl, amitrole, ammonium sulfamate, anilofos, anisuron, asulam, atraton, atrazine, azafenidin, azimsulfuron, aziprotryne, barban, BCPC, beflubutamid, benazolin, bencarbazone, benfluralin, benfuresate, bensulfuron-methyl, bensulide, benthicarb, bentazon, bentazone, bentazon-sodium, benzadox, benzfendazole, benzipram, benzobicyclon, benzofenap, benzofluor, benzoylprop, benzthiazuron, bicyclopiron, bifenox, bilanafos, bispyribac-sodium, borax, bromacil, bromobonil, bromobutide, bromofenoxim, bromoxynil, brompyrazon, butachlor, butafenacil, butamifos, butenachlor, buthidazole, buthiuron, butralin, butoxydim, buturon, butylate, cacodylic acid, cafenstrole, calcium chlorate, calcium cyanamide, cambendiclor, carbasulam, carbetamide, carboxazole chlorprocarb, carfentrazone-ethyl, CDEA, CEPC, chlomethoxyfen, chloramben, chloranocryl, chlorazifop, chlorazine, chlorbromuron, chlorbufam, chloreturon, chlorfenac, chlorfenprop,

chlorflurazole, chlorflurenol, chloridazon, chlorimuron, chlornitrofen, chloropon,
 chlorotoluron, chloroxuron, chloroxynil, chlorpropham, chlorsulfuron, chlorthal,
 chlorthiamid, cinidon-ethyl, cinmethylin, cinosulfuron, cisanilide, clethodim, clidinate,
 clodinafop-propargyl, clofop, clomazone, clomeprop, cloprop, cloproxydim, clopyralid,
 5 cloransulam-methyl, CMA, copper sulfate, CPMF, CPPC, credazine, cresol, cumyluron,
 cyanatryn, cyanazine, cycloate, cyclosulfamuron, cycloxydim, cycluron, cyhalofop-butyl,
 cyperquat, cyprazine, cyprazole, cypromid, daimuron, dalapon, dazomet, delachlor,
 desmedipham, desmetryn, di-allate, dicamba, dichlobenil, dichloralurea, dichlormate,
 dichlorprop, dichlorprop-P, diclofop-methyl, diclosulam, diethamquat, diethatyl,
 10 difenopenten, difenoxuron, difenzoquat, diflufenican, diflufenzopyr, dimefuron,
 dimepiperate, dimethachlor, dimethametryn, dimethenamid, dimethenamid-P, dimexano,
 dimidazon, dinitramine, dinofenate, dinoprop, dinosam, dinoseb, dinoterb, diphenamid,
 dipropetryn, diquat, disul, dithiopyr, diuron, DMPA, DNOC, DSMA, EBEP, eglinazone,
 endothal, epronaz, EPTC, erbon, esprocarb, ethalfluralin, ethametsulfuron, ethidimuron,
 15 ethiolate, ethofumesate, ethoxyfen, ethoxysulfuron, etinofen, etnipromid, etobenzanid, EXD,
 fenasulam, fenoprop, fenoxaprop, fenoxaprop-P-ethyl, fenoxaprop-P-ethyl + isoxadifen-
 ethyl, fenoxasulfone, fenteracol, fenthiafop, fentrazamide, fenuron, ferrous sulfate,
 flamprop, flamprop-M, oryzalin, florasulam, fluazifop, fluazifop-P-butyl, fluazolate,
 flucarbazone, flucetosulfuron, fluchloralin, flufenacet, flufenican, flufenpyr-ethyl,
 20 flumetsulam, flumezin, flumiclorac-pentyl, flumioxazin, flumipropyn, fluometuron,
 fluorodifen, fluoroglycofen, fluoromidine, fluoronitrofen, fluothiuron, flupoxam, flupropacil,
 flupropanate, flupyrsulfuron, fluridone, flurochloridone, fluroxypyr, flurtamone, fluthiacet,
 fomesafen, foramsulfuron, fosamine, furyloxyfen, glufosinate, glufosinate-ammonium,
 glufosinate-P-ammonium, glyphosate esters and salts, halosafen, halosulfuron-methyl,
 25 haloxydine, haloxyfop-methyl, haloxyfop-P-methyl, hexachloroacetone, hexaflurate,
 hexazinone, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr,
 imazosulfuron, indanofan, indaziflam, iodobonil, iodomethane, iodosulfuron, ioxynil,
 ipazine, ipfencarbazone, iprymidam, isocarbamid, isocil, isomethiozin, isonoruron,
 isopolinate, isopropalin, isoproturon, isouron, isoxaben, isoxachlortole, isoxaflutole,
 30 isoxapyrifop, karbutilate, ketospiradox, lactofen, lenacil, linuron, MAA, MAMA, MCPA
 esters and salts, MCPA-thioethyl, MCPB, mecoprop, mecoprop-P, medinoterb, mefenacet,
 mefluidide, mesoprazine, mesosulfuron, mesotrione, metam, metamifop, metamitron,
 metazachlor, metazosulfuron, metflurazon, methabenzthiazuron, methalpropalin, methazole,
 methiobencarb, methiozolin, methiuron, methometon, methoprotryne, methyl bromide,

methyl isothiocyanate, methyldymron, metobenzuron, metobromuron, metolachlor,
 metosulam, metoxuron, metribuzin, metsulfuron-methyl, molinate, monalide, monisouron,
 monochloroacetic acid, monolinuron, monuron, morfamquat, MSMA, naproanilide,
 napropamide, naptalam, neburon, nicosulfuron, nipyraclufen, nitralin, nitrofen, nitrofluorfen,
 5 norflurazon, noruron, OCH, orbencarb, *ortho*-dichlorobenzene, orthosulfamuron, oryzalin,
 oxadiargyl, oxadiazon, oxapyrazon, oxasulfuron, oxaziclomefone, oxyfluorfen, paraflufen-
 ethyl, parafluron, paraquat, pebulate, pelargonic acid, pentachlorophenol, pentanochlor,
 pentoxazone, perfluidone, pethoxamid, phenisopham, phenmedipham, phenmedipham-ethyl,
 phenobenzuron, phenylmercury acetate, picloram, picolinafen, pinoxaden, piperophos,
 10 potassium arsenite, potassium azide, potassium cyanate, pretilachlor, primisulfuron-methyl,
 procyazine, prodiamine, profluazol, profluralin, profoxydim, proglinazine, prometon,
 prometryn, pronamide, propachlor, propanil, propaquizafop, propazine, propham,
 propisochlor, propoxycarbazone, propyrisulfuron, propyzamide, prosulfalin, prosulfocarb,
 prosulfuron, proxan, prynachlor, pydanon, pyraclonil, pyraflufen-ethyl, pyrasulfotole,
 15 pyrazogyl, pyrazolynate, pyrazosulfuron-ethyl, pyrazoxyfen, pyribenzoxim, pyributicarb,
 pyriclor, pyridafol, pyridate, pyriftalid, pyriminobac, pyrimisulfan, pyrithiobac-sodium,
 pyroxasulfone, pyroxsulam, quinclorac, quinmerac, quinoclamine, quinonamid, quizalofop,
 quizalofop-P-ethyl, rhodethanil, rimsulfuron, saflufenacil, S-metolachlor, sebuthylazine,
 secbumeton, sethoxydim, siduron, simazine, simeton, simetryn, SMA, sodium arsenite,
 20 sodium azide, sodium chlorate, sulcotrione, sulfallate, sulfentrazone, sulfometuron, sulfosate,
 sulfosulfuron, sulfuric acid, sulglycapin, swep, TCA, tebutam, tebuthiuron, tefuryltrione,
 tembotrione, tepraloxym, terbacil, terbucarb, terbutylchlor, terbumeton, terbuthylazine,
 terbutryn, tetrafluron, thenylchlor, thiazafuron, thiazopyr, thidiazimin, thidiazuron,
 thiencarbazone-methyl, thifensulfuron-methyl, thiobencarb, tiocarbamil, tioclorim,
 25 topramezone, tralkoxydim, triafamone, tri-allate, triasulfuron, triaziflam, tribenuron-methyl,
 tricamba, triclopyr choline salt, esters and amines, tridiphane, trietazine, trifloxysulfuron,
 trifluralin, triflusulfuron, trifop, trifopsime, trihydroxytriazine, trimeturon, tripropindan, tritac
 tritosulfuron, vernolate, xylachlor and salts and esters, optically active isomers and mixtures
 thereof.

30 The synergistic mixture of the present invention can additionally be employed to
 control undesirable vegetation in many crops that have been made tolerant to or resistant to
 them or to other herbicides by genetic manipulation or by mutation and selection. The
 synergistic composition of the present invention can, further, be used in conjunction with 2,4-

D, glyphosate, glufosinate, dicamba, sulfonyleureas or imidazolinones on 2,4-D tolerant, glyphosate-tolerant, glufosinate-tolerant, dicamba-tolerant, sulfonyleurea-tolerant crops or imidazolinone-tolerant crops.

It is generally preferred to use the synergistic composition of the present invention 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. It is further generally preferred to apply the synergistic composition of the present invention and other complementary herbicides at the same time, either as a combination formulation or as a tank mix.

The synergistic composition of the present invention can generally be employed in combination with known herbicide safeners, such as benoxacor, benthocarb, brassinolide, cloquintocet (mexyl), cyometrinil, cyprosulfamate, daimuron, dichlormid, dicyclonon, dietholate, dimepiperate, disulfoton, fenchlorazole-ethyl, fencloirim, flurazole, fluxofenim, furilazole, harpin proteins, isoxadifen-ethyl, mefenpyr-diethyl, mephenate, MG 191, MON 4660, naphthalic anhydride (NA), oxabetrinil, R29148 and *N*-phenyl-sulfonylbenzoic acid amides, to enhance their selectivity.

In practice, it is preferable to use the synergistic composition of the present invention in mixtures containing an herbicidally effective amount of the herbicidal components along with at least one agriculturally acceptable adjuvant or carrier. Suitable adjuvants or carriers should not be phytotoxic to valuable crops, particularly at the concentrations employed in applying the compositions for selective weed control in the presence of crops, and should not react chemically with herbicidal components or other composition ingredients. Such mixtures can be designed for application directly to weeds or their locus or can be concentrates or formulations that are normally diluted with additional carriers and adjuvants before application. They can be solids, such as, for example, dusts, granules, water dispersible granules, or wettable powders, or liquids, such as, for example, emulsifiable concentrates, solutions, emulsions or suspensions.

Suitable agricultural adjuvants and carriers that are useful in preparing the herbicidal mixtures of the invention are well known to those skilled in the art. Some of these 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; C₉-C₁₁ alkylpolyglycoside; phosphated alcohol ethoxylate; natural primary alcohol (C₁₂-C₁₆) ethoxylate; di-*sec*-butylphenol EO-PO block copolymer; polysiloxane-methyl cap; nonylphenol ethoxylate + urea ammonium nitrate; emulsified methylated seed oil; tridecyl
5 alcohol (synthetic) ethoxylate (8EO); tallow amine ethoxylate (15 EO); PEG(400) dioleate-99.

Liquid carriers that can be employed include water and organic solvents. The organic solvents typically used include, but are not limited to, petroleum fractions or hydrocarbons such as mineral oil, aromatic solvents, paraffinic oils, and the like; vegetable oils such as
10 soybean oil, rapeseed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; esters of the above vegetable oils; esters of monoalcohols or dihydric, trihydric, or other lower polyalcohols (4-6 hydroxy containing), such as 2-ethyl hexyl stearate, *n*-butyl oleate, isopropyl myristate, propylene glycol dioleate, di-octyl succinate, di-butyl adipate, di-octyl
15 phthalate and the like; esters of mono, di and polycarboxylic acids and the like. Specific organic solvents include 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
20 glycol, glycerine, *N*-methyl-2-pyrrolidinone, *N,N*-dimethyl alkylamides, dimethyl sulfoxide, liquid fertilizers and the like. Water is generally the carrier of choice for the dilution of concentrates.

Suitable solid carriers include talc, pyrophyllite clay, silica, attapulgus clay, kaolin clay, kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite clay, Fuller's
25 earth, cottonseed hulls, wheat flour, soybean flour, pumice, wood flour, walnut shell flour, lignin, and the like.

It is usually desirable to incorporate one or more surface-active agents into the compositions of the present invention. Such surface-active agents are advantageously employed in both solid and liquid compositions, especially those designed to be diluted with
30 carrier before application. The surface-active agents can be anionic, cationic or nonionic in character and can be employed as emulsifying agents, wetting agents, suspending agents, or for other purposes. Surfactants conventionally used in the art of formulation and which may

also be used in the present formulations are described, *inter alia*, in “McCutcheon’s Detergents and Emulsifiers Annual,” MC Publishing Corp., Ridgewood, New Jersey, 1998 and in “Encyclopedia of Surfactants,” Vol. I-III, Chemical Publishing Co., New York, 1980-81. Typical surface-active agents include salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; alkylarylsulfonate salts, such as calcium dodecylbenzenesulfonate; alkylphenol-alkylene oxide addition products, such as nonylphenol-C₁₈ ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol-C₁₆ ethoxylate; soaps, such as sodium stearate; alkylnaphthalene-sulfonate salts, such as sodium dibutyl-naphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryl trimethylammonium chloride; polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; salts of mono- and dialkyl phosphate esters; vegetable or seed oils such as soybean oil, rapeseed/canola oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; and esters of the above vegetable oils, particularly methyl esters.

Oftentimes, some of these materials, such as vegetable or seed oils and their esters, can be used interchangeably as an agricultural adjuvant, as a liquid carrier or as a surface active agent.

Other adjuvants commonly used in agricultural compositions include compatibilizing agents, antifoam agents, sequestering agents, neutralizing agents and buffers, corrosion inhibitors, dyes, odorants, spreading agents, penetration aids, sticking agents, dispersing agents, thickening agents, freezing point depressants, antimicrobial agents, and the like. The compositions may also contain other compatible components, for example, other herbicides, plant growth regulants, fungicides, insecticides, and the like and can be formulated with liquid fertilizers or solid, particulate fertilizer carriers such as ammonium nitrate, urea and the like.

The concentration of the active ingredients in the synergistic composition of the present invention is generally from 0.001 to 98 percent by weight. Concentrations from 0.01 to 90 percent by weight are often employed. In compositions designed to be employed as concentrates, the active ingredients are generally present in a concentration from 1 to 98 weight percent, preferably 2 to 90 weight percent. Such compositions are typically diluted

with an inert carrier, such as water, before application. The diluted compositions usually applied to weeds or the locus of weeds generally contain 0.0001 to 1 weight percent active ingredient and preferably contain 0.001 to 0.05 weight percent.

The present compositions can be applied to weeds or their locus by the use of conventional ground or aerial dusters, sprayers, and granule applicators, by addition to irrigation water, and by other conventional means known to those skilled in the art.

The following examples illustrate the present invention.

Examples

Evaluation of Preemergence Herbicidal Activity of Mixtures under Field Conditions

10 Methodology

Field trials were conducted in rice and tree crops using standard herbicide small plot research methodology. Plot size was typical for small plot research, varying from 2 to 4 meters (m) wide by 6.7 to 10 meters long. There were 3 to 4 replicates per treatment. Soil types ranged from medium to fine soil texture. Rice or cereal crops were sown by mechanical direct dry seeding as per normal local cultural practices. The rice or cereal crop was grown using normal cultural practices for fertilization, watering, flooding and maintenance to ensure good growth of the crop and the weeds.

Treatments were applied by backpack sprayer using either compressed air or CO₂, at spray pressures from 124 to 276 kilopascals (kPa). Spray tips were typically Flat Fan Teejet nozzles, such as TJ8002 to TJ110015 or XR11001. Spray volumes varied from 93.5 to 250 liters per hectare (L/ha). Penoxsulam was applied as the commercial products Grasp SC (240 gr ai/L) or Clipper 20 OD (20 grams ai/L); pendimethalin was applied as the commercial product Prowl EC.

For each treatment, the appropriate formulated product amount to treat the plot area, to achieve the desired application rate, based on unit area of application (hectare), was calculated, measured, and mixed in water prior to applying with the backpack sprayer. Treatments were rated as compared to the untreated control plots.

Evaluation

The treated plots and control plots were rated blind at various intervals after application. Ratings were based of Percent (%) Visual weed control, where 0 corresponds to no injury and 100 corresponds to complete kill.

5 Data were collected for all trials and analyzed using various statistical methods.

Colby's equation was used to determine the herbicidal effects expected from the mixtures (Colby, S. R. Calculation of the synergistic and antagonistic response of herbicide combinations. *Weeds* **1967**, 15, 20-22).

10 The following equation was used to calculate the expected activity of mixtures containing two active ingredients, A and B:

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

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

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

The results are summarized in Tables 1 through 3.

Table1. Synergistic broadleaf weed control at 22 to 54 days after application from
Penoxsulam + Pendimethalin applied preemergence to seeded rice - Field trials.

Application Rate (gai/ha)		% Visual Control					
		ALRPH		IPOSS		SEBEX	
Penoxsulam	Pendimethalin	Obs	Ex	Obs	Ex	Obs	Ex
20 (1)	0	43	-	-	-	-	-
0	1100	0	-	-	-	-	-
20	1100	76	43	-	-	-	-
20 (2)	0	74	-	21	-	-	-
0	1100	0	-	35	-	-	-
20	1100	100	74	83	49	-	-
40	0	-	-	-	-	40	-
0	1100	-	-	-	-	14	-
40	1100	-	-	-	-	86	47

5

(1) = Arkansas, USA

(2) = Texas, USA

ALRPH = *Alternanthera philoxeroides* (alligatorweed)IPOSS = *Ipomoea* spp. (morningglory)SEBEX = *Sesbania exaltata* (hemp sesbania/coffeeweed)

10

Obs = Observed results

Ex = Expected results

gai/ha = grams of active ingredient per hectare

15

Table 2. Synergistic grass weed control at 60 days after application from Penoxsulam + Pendimethalin applied preemergence to seeded rice - Field trials.

Application Rate (gai/ha)		% Visual Control			
		ECHCO		ISCRU	
Penoxsulam	Pendimethalin	Obs	Ex	Obs	Ex
20	0	25	-	-	-
0	750	55	-	-	-
20	750	93	66	-	-
30	0	-	-	35	-
0	750	-	-	57	-
30	750	-	-	96	73

5

ECHCO = *Echinochloa colonum* (junglerice)ISCRU = *Ischaemum rugosum* (saramollagrass)

Obs = Observed results

Ex = Expected resultsgai/ha = grams of active ingredient per hectare

10

Table 3. Synergistic grass weed control at 206 days after application from Penoxsulam + Pendimethalin applied preemergence to perennial tree crops - Field trials.

		% Control	
Application Rate (gai/ha)		ALOMY	
Penoxsulam	Pendimethalin	Obs	Ex
10	0	0	-
0	500	0	-
10	500	63	0
20	0	20	-
0	500	0	-
20	500	82	20
30	0	43	-
0	500	0	-
30	500	84	43
10	0	0	-
0	1000	7	-
10	1000	87	7
20	0	20	-
0	1000	7	-
20	1000	94	25
30	0	43	-
0	1000	7	-
0	1000	97	47
40	0	50	-
0	1000	7	-
40	1000	95	53

5 ALOMY = *Alopecurus myosuroides* (blackgrass)
 Obs = Observed results
 Ex = Expected results
 gai/ha = grams of active ingredient per hectare

10

WHAT IS CLAIMED IS:

1. A synergistic herbicidal composition comprising a herbicidally effective amount of (a) penoxsulam and (b) pendimethalin.

2. The composition of claim 1, wherein the weight ratio of pendimethalin to penoxsulam on an active ingredient (ai) basis is between about 224:1 and about 3:1.

3. The composition of claim 1, wherein the weight ratio of pendimethalin to penoxsulam on an active ingredient (ai) basis is between about 55:1 and about 17:1.

4. The composition of claim 1, further comprising an agriculturally acceptable adjuvant or carrier.

5. A method of controlling undesirable vegetation which comprises contacting the vegetation or the locus thereof with a herbicidally effective amount the composition of claim 1.

6. The method of claim 5, wherein the composition is applied at an application rate between about 130 gai/ha and about 2290 gai/ha.

7. The method of claim 5, wherein the composition is applied at an application rate between about 180 gai/ha and about 1730 gai/ha.

8. The method of claim 5, wherein the pendimethalin is applied at a rate between about 500 gai/ha and about 1100 gai/ha and the penoxsulam is applied at a rate between about 10 gai/ha and about 40 gai/ha.

9. The method of claim 5, wherein the undesirable vegetation is alligator weed, morning glory, coffeeweed, junglerice, saramollagrass, or blackgrass.

10. A method of controlling undesirable vegetation in a crop, comprising contacting the vegetation or the locus thereof with a herbicidally effective amount the composition of claim 1, wherein the crop is rice, cereal, grain, turf, IVM, sugar cane or tree and vine orchard.

5

11. The method of claim 10 in which the composition of claim 1 is applied preemergence to early postemergence to the undesirable vegetation.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/43526

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 27/14 (2012.01)

USPC - 504/200

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)- B01J 27/14 (2012.01);

USPC- 504/200

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and NPL (classification, keyword; search terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (US Pat, PgPub, EPO, JPO), GoogleScholar (PL, NPL), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL);
search terms: penoxsulam, pendimethalin, rice, cereal, grain, turf, sugar cane, tree, vine, orchard, alligator weed, morning glory, coffee weed, jungle rice, saramolla grass, black grass

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Grasp SC, "Versatile and Reliable New Tool for Rice Protection." Datasheet [online]. Dow AgroSciences, 2008 [Retrieved on 2012-08-13]. Retrieved from the Internet: <URL: http://www.dowagro.com/PublishedLiterature/dh_00dc/0901b803800dcdd2.pdf?filepath=usag/pdfs/noreg/010-31598.pdf&fromPage=GetDoc >, see entire document, especially pg 1	1
X	US 2006/0183637 A1 (LOUGHNER et al.) 17 August 2006 (17.08.2006), para [0003], [0004], [0010]-[0014]	1-11
A	US 2008/0153704 A1 (YAMAJI et al.) 26 June 2008 (26.06.2008), para [0014], [0032], [0112], [0163], [0189]	1-11

☐ 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

13 August 2012 (13.08.2012)

Date of mailing of the international search report

31 AUG 2012

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. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774