(12) STANDARD PATENT (11) Application No. **AU 2006338192 B2**
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Solventless formulation of triclopyr butoxyethyl ester

(51) International Patent Classification(s)
A01N 43/40 (2006.01) ***A01N 25/30*** (2006.01)
A01N 25/04 (2006.01) ***A01P 13/00*** (2006.01)

(21) Application No: **2006338192** (22) Date of Filing: **2006.11.17**

(87) WIPO No: **WO07/094836**

(30) Priority Data

(31) Number	(32) Date	(33) Country
60/773,417	**2006.02.15**	**US**

(43) Publication Date: **2007.08.23**
(44) Accepted Journal Date: **2012.03.22**

(71) Applicant(s)
Dow AgroSciences LLC

(72) Inventor(s)
Hailu, Alefesh;Kline III, William N.;Jensen, Jeffrey Lee;Burch, Patrick L.;Troth, John L.;Pompeo, Michael P.

(74) Agent / Attorney
Freehills Patent & Trade Mark Attorneys, Level 43 101 Collins Street, Melbourne, VIC, 3000

(56) Related Art
BEBAWI, F.F. et al, Plant Protection Quarterly, 1999, vol. 14, no. 2, pages 57-62
WO 2004/093546 A1
AU 2004/100006 A4

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 August 2007 (23.08.2007)

PCT

(10) International Publication Number
WO 2007/094836 A1

(51) International Patent Classification:
A01N 43/40 (2006.01) *A01N 25/04* (2006.01)
A01N 25/30 (2006.01) *A01P 13/00* (2006.01)

(21) International Application Number:
PCT/US2006/044751

(22) International Filing Date:
17 November 2006 (17.11.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/773,417 15 February 2006 (15.02.2006) US

(71) Applicant *(for all designated States except US)*: **DOW AGROSCIENCES LLC** [US/US]; 9330 Zionsville Road, Indianapolis, IN 46268-1054 (US).

(71) Applicant and
(72) Inventor *(for all designated States except US)*: **JENSEN, Jeffrey, Lee** [US/US]; 8906 North County Road 1050 East, Brownsburg, IN 46112 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **KLINE, William, N., III** [US/US]; 2716 Saxon Drive, Duluth, GA 30096 (US). **BURCH, Patrick, L.** [US/US]; 3425 Elk Creek Drive, Christiansburg, VA 24073 (US). **TROTH, John, L.** [US/US]; 11229 Lakeshore Drive West, Carmel, IN 46033 (US). **HAILU, Alefesh** [US/US]; 6834 Perinwood Drive, Cincinnati, OH 45248 (US). **POMPEO, Michael, P.** [US/US]; 925 Windrow Court, Sumter, SC 29150 (US).

(74) Agent: **MIXAN, Craig, E.**; Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, IN 46268 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, 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, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/094836 A1

(54) **Title:** SOLVENTLESS FORMULATION OF TRICLOPYR BUTOXYETHYL ESTER

(57) **Abstract:** A solventless herbicidal composition of triclopyr butoxyethyl ester and a surfactant provides efficient control of woody plants while reducing exposure to aromatic carriers.

SOLVENTLESS FORMULATION OF TRICLOPYR BUTOXYETHYL ESTER

This application claims priority, under 35 U.S.C. §119(e), of U.S. Provisional Patent Application No. 60/773,417, filed on February 15, 2006. This invention concerns a novel triclopyr butoxyethyl ester composition.

Today's increased attention to nature and the environment has resulted in unprecedented efforts to encourage grasses, low-growing ground cover, and wildflowers on rights-of-way. In electric utility rights-of-way, tall growing tree and shrub species interfere with electrical line maintenance operations and if left uncontrolled can result in trees growing into power lines, resulting in power outages. On roadside rights of way, tall growing weeds interfere with water drainage from the road edge, resulting in more frequent need for road maintenance, restrict ability of motorists to use the road shoulder, cause poor vision along the right-of-way and contribute to spread of untreated noxious weed species into adjacent crop lands. In forest lands, removal of unwanted tall growing trees and woody shrubs is a frequent forest management practice in order to encourage growth of desirable tree species. Thus control treatments are required to remove tall-growing woody plants in vegetation control programs. Not only do such treatment programs result in effective, long lasting brush control, they leave non-target plants virtually untouched. This allows desired plants to thrive because they are freed from competition for moisture, nutrients and sunlight.

One such treatment program consists of the use of basal bark or stem application of an herbicide to control undesired vegetation. This particular method is attractive because it provides not only vegetation control but also efficient placement and utilization of the herbicide composition on individual plants. U.S. Patent 5,466,659 describes this method of treatment with a variety of triclopyr

butoxyethyl ester compositions. Another such treatment program consists of the use of a foliar application of an herbicide to control undesired vegetation. This particular method is attractive because it provides not only vegetation control but, when a selective herbicide is used, desirable vegetation is encouraged.

In order to have the herbicide penetrate into the woody plant, it is desirable to dissolve the herbicide in a non-aqueous organic carrier. As currently used, as in Garlon™ 4 herbicide, for example, such carriers consists of petroleum distillates such as fuel oils, e.g., diesel oil or kerosene.

However, these carriers present risks not only to the surrounding environment, but also to the applicator as well. In aerial applications, for example, due to applicator technique or wind conditions, over-spray onto surrounding areas may result in unplanned deposition of the carriers during the application.

The present invention concerns an herbicidal composition consisting essentially of 70 to 95 weight percent triclopyr butoxyethyl ester and 5 to 30 weight percent of a surfactant. A preferred surfactant comprises a mixture of 25 to 65 weight percent of an alkylbenzenesulfonate salt, 25 to 45 weight percent of an ethylene oxide-propylene oxide block copolymer and 15 to 35 weight percent of an ethoxylated-propoxylated fatty alcohol. Another aspect of the present invention concerns a method for controlling undesired woody vegetation which comprises applying to the foliage or to the basal bark or stem of the woody vegetation an aqueous dilution of the herbicidal composition. In addition to providing for more efficient treatment procedures, i.e., both foliar and basal bark applications, and providing reduced exposure to aromatic carriers, the present composition provides unexpected improved control of a number of key woody plants.

This invention provides a solventless herbicidal composition consisting essentially of triclopyr butoxyethyl ester and a surfactant.

Triclopyr is the common name for 3,5,6-trichloro-2-pyridinyloxyacetic acid. This compound is a selective systemic herbicide used in the control of brush and woody vegetation, and many broad-leaved weeds, in areas such as grasslands and other uncultivated lands, industrial areas, rights-of-way, coniferous forests and crops including oil palm and rubber plantations and rice.

The butoxyethyl ester of triclopyr is commercially available from Dow AgroSciences as Garlon™ 4 herbicide, a 4 lb acid equivalents/gallon formulation containing petroleum distillates as solvents and carriers for the active ingredient, triclopyr.

The surfactant of the present invention can be anionic, cationic or nonionic in character. Typical surfactants include salts of alkyl sulfates, such as diethanol-ammonium lauryl sulfate; alkylarylsulfonate salts, such as calcium dodecyl-benzenesulfonate; alkylphenol-alkylene oxide addition products, such as nonylphenol-C_{18} ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol-C_{16} ethoxylate; soaps, such as sodium stearate; alkyl-naphthalenesulfonate salts, such as sodium dibutylnaphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl) sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryl trimethyl-ammonium chloride; polyethylene glycol esters of fatty acids, such as poly-ethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; salts of mono and dialkyl phosphate esters; and mixtures thereof.

A preferred surfactant used in the solventless composition of the present invention is a mixture of an alkylbenzene sulfonate salt, a block copolymer of ethylene oxide and propylene oxide and an ethoxylated-propoxylated fatty alcohol.

The alkylbenzene sulfonate salt preferably comprises from 25 to 65 and more preferably from 30 to 60 weight percent of the surfactant mixture (based on

the active substances). Suitable alkylbenzene sulfonate salts include the alkaline earth metal, ammonium, amine, alkanolamine salt of an alkylbenzene sulfonate. Preferably, the alkylbenzene sulfonate comprises an alkyl group containing from 8 to 22 carbon atoms. Preferably, the anionic surfactant comprises a calcium or magnesium salt of an alkylbenzene sulfonate and most preferably the calcium salt. The most preferred alkylbenzene sulfonate is the calcium salt of dodecylbenzene sulfonate.

The block copolymer of ethylene oxide and propylene oxide, which may be capped or started at least at one end with an aliphatic, aromatic or cycloaliphatic moiety, comprises from 25 to 45 weight percent of the surfactant mixture. Preferably, an ethylene oxide-propylene oxide block copolymer is started with an aryl or aliphatic group which may be cyclic. Block copolymers of ethylene oxide and propylene oxide ranging from 5 to 25 ethylene oxide units and from 20 to 40 propylene oxide units are suitable with 10 to 20 ethylene oxide units and from 25 to 35 propylene oxide units being preferred.

The ethoxylated-propoxylated fatty alcohol comprises from 15 to 35 weight percent of the surfactant mixture. C_{10}-C_{18} Fatty alcohols or mixtures thereof are suitable with C_{12}-C_{14} fatty alcohols generally preferred. The fatty alcohols are ethoxylated and propoxylated with ethylene oxide and propylene oxide ranging from 1 to 10 ethylene oxide units and from 1 to 15 propylene oxide units, with 1 to 5 ethylene oxide units and from 5 to 10 propylene oxide units being preferred. The ethylene oxide and the propylene oxide units may be block or random.

The compositions of the present invention contain from 70 to 95 weight percent of triclopyr butoxyethyl ester and from 5 to 30 weight percent of surfactant mixture. Preferably the composition contains from 80 to 90 weight percent of

triclopyr butoxyethyl ester and from 10 to 20 weight percent of surfactant mixture.

In addition to the compositions and uses set forth above, the present invention also embraces the composition and use of these triclopyr butoxyethyl ester compositions in combination with one or more additional compatible ingredients. Other additional ingredients may include, for example, one or more other herbicides, dyes, and any other additional ingredients providing functional utility, such as, for example, stabilizers, fragrants, viscosity-lowering additives, and freeze-point depressants.

Additional herbicidal compounds employed as supplements or additives should not be antagonistic to the activity of the triclopyr butoxyethyl ester composition as employed in the present invention. Suitable herbicidal compounds include, but are not limited to 2,4-D, 2,4-MCPA, ametryn, aminopyralid, asulam, atrazine, butafenacil, carfentrazone-ethyl, chlorflurenol, chlormequat, chlorpropham, chlorsulfuron, chlortoluron, cinosulfuron, clethodim, clopyralid, cyclosulfamuron, DE-742, dicamba, dichlobenil, dichlorprop-P, diclosulam, diflufenican, diflufenzopyr, diuron, fluroxypyr, glyphosate, hexazinone, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, MCPA, metsulfuron-methyl, picloram, pyrithiobac-sodium, sethoxydim, sulfometuron, sulfosate, sulfosulfuron, tebuthiuron, terbacil, thiazopyr, thifensulfuron, triasulfuron and tribenuron.

Particularly useful herbicidal compounds for use with triclopyr butoxyethyl ester in foliar brush-control applications are clopyralid esters and amines, e.g., 3,6-dichloro-2-pyridinecarboxylic acid monoethanolamine salt, as well as mixtures with fluroxypyr 1-methylheptyl ester, with aminopyralid salts, with 2,4-D butoxyethyl ester or 2-ethylhexyl ester, and with picloram *iso*-octyl ester. The herbicidal composition used in the method of the present invention can be

2006338192 21 Sep 2011

formulated with the other herbicide or herbicides, tank mixed with the other herbicide or herbicides, or applied sequentially with the other herbicide or herbicides.

Dyes may be used in the formulated composition as a marker. Generally, a preferred dye can be any oil-soluble dye selected from EPA's approved list of inerts exempt from tolerance. Such dyes, may include, for example, D&C Red #17, D&C Violet #2, and D&C Green #6. Dyes are generally added to the composition by adding the desired amount of dye to the formulated composition with agitation. Dyes are generally present in the final formulation composition in a concentration of 0.1-1.0 percent by weight.

As used herein, except where the context requires otherwise, the term "comprise" and variations of the term, such as "comprising", "comprises" and "comprised", are not intended to exclude other additives, components, integers or steps.

Reference to any prior art in the specification is not, and should not be taken as, an acknowledgment or any form of suggestion that this prior art forms part of the common general knowledge in Australia or any other jurisdiction.

The compositions of the present invention are diluted with water prior to being applied to the foliage of the woody vegetation. The diluted compositions usually applied to the woody vegetation generally contain 0.0001 to 20.0 weight percent triclopyr butoxyethyl ester.

The following examples illustrate the present invention.

Example 1 Preparation of Surfactant Mixture.

Agnique™ ABS 60C – dodecylbenzene sulfonate calcium salt (60 percent active) – (50 g) was warmed to 40°C. While stirring, molten (35°C) Agnique™ BP NP-1530-nonylphenol block copolymer PO(30) EO(15) – (30 g) and then Dehypon™ LS 36 – C_{12}-C_{14} fatty alcohol PO(6) EO(3) – (20 g) was added. The mixture was stirred until a single phase was obtained.

Example 2 Preparation of Ticlopyr Butoxyethyl Ester Formulation

The surfactant mixture from Example 1 (14 g), was added with stirring at room temperature to 86 g of technical triclopyr butoxyethyl ester. Stirring was

continued until a single phase was obtained.

Example 3 Herbicidal Testing

Trials were conducted at four locations in mixed and single species woody plant sites. Target woody brush was six feet or less and application was conducted over the top with hand held booms. The study was designed to compare the solventless formulation of Example 2 to the commercially available Garlon 4 formulation that contains kerosene. The rates selected were based on the target species. In mixed brush, the rates were 1.5 and 3.0 pounds acid equivalents per acre (lbs ae/ac) (1.68 and 3.36 kilogram acid equivalent per hectare (kg ae/ha)). For Scotch broom the rates were 1.25 lbs ae/ac (1.4 kg ae/ha). The formulations were diluted in water and applied at a delivery volume of 20 gallons per acre (gpa) (187 liters per hectare (L/ha)). No surfactant was added to the mixtures. Sites were treated in the growing season and assessment of control was made the following year. The results (percent control) are summarized in Table I.

Table I

Species Common Name	Solventless Formulation		Kerosene Garlon 4	
	1.25 lbae/ac (1.4 kgae/ha) Percent control		1.25 lbae/ac (1.4 kgae/ha) Percent control	
scotch broom	85		65	
	1.5 lbae/ac (1.68 kgae/ha) Percent control	3.0 lbae/ac (3.36 kgae/ha) Percent control	1.5 lbae/ac (1.68 kgae/ha) Percent control	3.0 lbae/ac (3.36 kgae/ha) Percent control
sweetgum	55	83	43	61
cherry	47	57	30	37
loblolly pine	13	63	26	40
red oak	50	77	47	58
water/willow oak	50	77	47	62

CLAIMS:

1. An herbicidal composition comprising 70 to 95 weight percent triclopyr butoxyethel ester and 5 to 30 weight percent of a surfactant, which comprises a mixture of 25 to 65 weight percent of an alkylbenzenesulfonate salt, 25 to 45 weight percent of an ethylene oxide-propylene oxide block copolymer and 15 to 35 weight percent of an ethoxylated-propoxylated fatty alcohol.

2. A method for controlling undesired woody vegetation which comprises applying to the foliage or to the basal bark or stem of the woody vegetation an aqueous dilution of the herbicidal composition of Claim 1.

3. The method of Claim 2 in which the herbicidal composition is used with an additional herbicide.

4. The method of Claim 3 in which the additional herbicide is aminopyralid clopyralid, fluroxypyr or picloram.

5. A herbicidal composition according to Claim 1 which further includes one or more compatible ingredients selected from the group consisting of dyes, and any other additional ingredients providing functional utility, such as, for example, stabilizers, fragrants, viscosity-lowering additives, and freeze-point depressants.

6. A herbicidal composition according to Claim 1 substantially as hereinbefore described with reference to Example 1 or 2.