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- (71) **Applicant:** HUNTSMAN PETROCHEMICAL LLC
[US/US]; 10003 Woodloch Forest Drive, The Woodlands,
TX 77380 (US).
- (72) **Inventors:** STERN, Alan, J.; 5925 Ranch Lake, Magnolia,
TX 77354 (US). FERGUSON, Dave, C.; 6663 Knoll-
bridge Lane, Spring, TX 77379 (US).
- (74) **Agent:** KOROMPAI, Edward, D.; Huntsman International
LLC, Legal Department, 10003 Woodloch Forest Drive,
The Woodlands, TX 77380 (US).
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(54) **Title:** EMULSIFIABLE CONCENTRATE FORMULATIONS OF CHLOROACETAMIDE AND HPPD INHIBITOR HERBICIDES

(57) **Abstract:** Emulsifiable concentrate preparations of HPPD inhibitor herbicides such as mesotrione in agriculturally acceptable solvents are disclosed. Carbonyl containing solvents such as alkylene carbonates are useful for dissolving such herbicides, along with other active ingredients such as anilide or chloracetamide herbicides, for example metolachlor. Such solvents enable preparation of emulsifiable concentrates of metolachlor and mesotrione that are stable over long periods of time at ambient temperatures.



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EMULSIFIABLE CONCENTRATE FORMULATIONS OF CHLOROACETAMIDE AND HPPD INHIBITOR HERBICIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of United States Provisional Patent Application Serial No. 61/684,472, filed August 17, 2012, which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

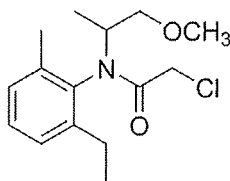
Field of the Invention

[0002] Embodiments described herein generally relate to herbicidal compositions. More specifically, useful compositions of HPPD inhibitor herbicides and anilide or chloroacetamide herbicides are disclosed.

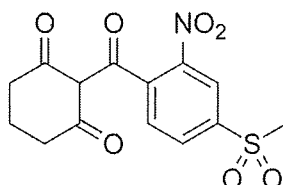
Description of the Related Art

[0003] Chloroacetamide herbicides have the general formula $RR'N-CO-C-Cl$. HPPD inhibitor herbicides take a number of forms, but generally act to suppress carotenoid biosynthesis by interrupting the function of hydroxyphenylpyruvate dioxygenase (HPPD), allowing destruction of chlorophyll by UV radiation. Interest has recently developed in using such herbicides together in a blend.

[0004] Metolachlor is an example of a chloroacetamide herbicide that has the formula



Metolachlor is also an example of an anilide herbicide due to the benzene ring attached to the amide structure. Mesotrione is an example of an HPPD inhibitor that has the formula



Because mesotrione is a relatively high-melting compound, commercially available blends of these two herbicides are currently of the suspoemulsion type, wherein the metolachlor is present as a liquid, emulsified in water, and the mesotrione is present as a suspended solid. Such formulations are very difficult to develop and tend to be unstable during long-term storage due to the difficulty of keeping the solid and oil phases suspended in the water.

[0005] Emulsifiable concentrates are a type of agricultural formulation in which the active ingredients are dissolved in a suitable solvent, with emulsifiers, such that when the concentrate is added to water an emulsion spontaneously forms. Such formulations are typically easy to manufacture, use, and store. Difficulties arise when an active ingredient is not readily soluble in an agriculturally acceptable solvent. High-melting solids, such as mesotrione, are prone to precipitate from solution at low temperatures. Consequently, there is no emulsifiable concentrate formulation of metolachlor and mesotrione available today. An emulsifiable concentrate formulation of metolachlor and mesotrione, and generally a way to make emulsifiable concentrates of chloroacetamide and HPPD-inhibitor herbicides, is needed.

SUMMARY OF THE INVENTION

[0006] Embodiments described herein include a composition that includes an emulsifiable concentrate of an HPPD inhibitor herbicide, such as mesotrione,

dissolved in an agriculturally acceptable solvent. The agriculturally acceptable solvent is usually a carbonyl containing compound, such as a ketone, ester, amide, organic carbonate, lactam, lactone, or urethane. An example is propylene carbonate. The composition may further include an anilide herbicide, such as metolachlor. In some cases, a co-solvent may also be used.

[0007] Other embodiments described herein include an emulsifiable concentrate herbicide composition with an HPPD inhibitor herbicide such as mesotrione, a chloroacetamide herbicide such as metolachlor, an alkylene carbonate such as propylene carbonate, butylene carbonate, and/or pentene carbonate, and a water immiscible co-solvent.

DETAILED DESCRIPTION

[0008] The inventors have discovered a class of agriculturally suitable solvents that can be used in the preparation of stable emulsifiable concentrates of metolachlor and mesotrione, and are expected to be generally usable for blends of anilide and HPPD inhibitor herbicides. Metolachlor and acetochlor are examples of the chloroacetamide class of anilide herbicides, while mesotrione and tembotrione are examples of HPPD inhibitor herbicides. The agriculturally suitable solvents that can be used in the preparation of stable emulsifiable concentrates of HPPD inhibitor herbicides are typically carbonyl containing liquids with a substantial dipole moment, for example having a dipole moment greater than about 2.5 D. Suitable solvents include alkylene carbonates such as ethylene carbonate, propylene carbonate, butylene carbonate, and pentene carbonate. Other suitable solvents include cyclohexanone, acetophenone, and gamma butyrolactone. The solvents used for the blend formulations described herein are typically not miscible with water, although some water solubility may be tolerated. Thus, small amounts of water soluble solvents such as N-methyl pyrrolidinone, dimethylformamide, and dimethylsulfoxide (DMSO) may be used.

[0009] Although the solvents described herein may be used alone, a co-solvent may also be used. When the primary solvent has some water solubility (for example propylene carbonate) or complete water solubility (for example N-methylpyrrolidinone), a co-solvent having very low water solubility may be used to moderate the water solubility of the primary solvent. The co-solvent, when used, is selected to promote dissolution of the active ingredients in the emulsifiable concentrate. Examples of suitable co-solvents include fatty acid dimethyl amides and fatty acid morpholine amides such as JEFFSOL[®] AG-1740 and JEFFSOL[®] AG-1730, available from Huntsman, LLC, of The Woodlands, Texas. Other co-solvents that may be used include aromatic petroleum distillates such as Aromatic 100, Aromatic 150, and Aromatic 200, available from ExxonMobil Chemical Company, of Houston, Texas. The total amount and ratio of the primary solvent and co-solvent in the formulation may vary according to factors such as presence and concentration of other herbicides or active ingredients and the amount of emulsifier employed.

[0010] The solvents described above will dissolve compounds such as mesotrione and tembotrione up to a concentration of about 10 wt% at ambient temperature, which is suitable for most agricultural applications. The solvents and formulations described herein are generally useful at a wide range of ambient conditions. Some formulations are usable at temperatures as low as 0°C (32°F). The desired temperature performance of the formulation depends on ambient conditions where the formulation will be used. Some useful solvents, such as ethylene carbonate, may be solid at ambient conditions. Such solvents may be used, nonetheless, by dissolving or dispersing the herbicide components in a co-solvent and then dissolving the solvent in the resulting liquid mixture.

[0011] Anilide herbicides such as metolachlor may dissolve in the solvents described herein up to a concentration of 50 wt% or more in most cases. An emulsifiable concentrate of an HPPD herbicide and an anilide herbicide may be

made by first dissolving both herbicide components in one or more of the polar solvents described herein, optionally adding a co-solvent, and adding a suitable blend of emulsifiers. Selecting an appropriate emulsifier is well known in the art. The HPPD herbicide, for example mesotrione, tembotrione, or tefuryltrione, may be present up to a concentration of about 10 wt%, such as between about 0.1 wt% and about 10 wt%, such as between about 2.0 wt% and about 5.0 wt%, for example about 4.0 wt%. The anilide herbicide, which may be a chloroacetamide herbicide such as metolachlor or acetochlor, may be present in a concentration between about 0 wt% and about 75 wt%, such as between about 20 wt% and about 60 wt%, for example about 50 wt%.

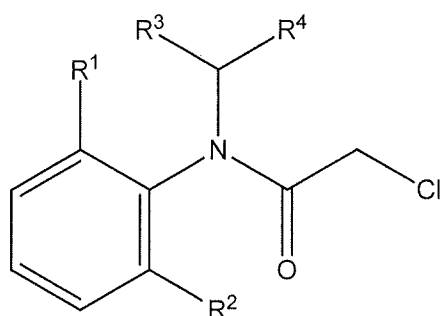
[0012] The alkylene carbonate solvents usable for the emulsifiable concentrates described herein include ethylene carbonate, propylene carbonate, butylene carbonate, and pentene carbonate. The butylene carbonate may be derived from primary butylene or isobutylene, or a mixture thereof, and the isobutylene carbonate may be cis or trans or any mixture thereof. The pentene carbonate may be derived from primary or isopentene, or any mixture thereof, and the isopentene carbonate may be cis or trans or any mixture thereof. The alkylene carbonate may also be a mixture of propylene, butylene, and/or pentene carbonates. Cyclopentene carbonate and cyclohexene carbonate may also be used, alone or in mixtures with the other carbonates described above.

[0013] For application, the emulsifiable concentrate is typically mixed with water to form an emulsion. A co-solvent may be useful in some cases to prevent or minimize precipitation of one or more active ingredients in the water phase. The co-solvent may be present in a concentration up to about 30%, such as between about 0% and about 25%, for example about 10%.

[0014] HPPD inhibitor herbicides for which compositions described herein may be useful include mesotrione and its benzoylcyclohexanedione variants sulcotrione, tefuryltrione, tembotrione, and ketospiradox. Other triketones, such as

bicyclopyrone and benzobicyclon may be useful HPPD inhibitors usable in the compositions described herein. Other useful benzoyl derivative triketones that may be dissolved by the solvents described herein to form emulsifiable concentrate solutions include 2-(2'-nitro-4'-methylsulphonylbenzoyl)-1,3-cyclohexanedione, 2-(2'-nitro-4'-methylsulphonyloxybenzoyl)-1,3-cyclohexanedione, 2-(2'-chloro-4'-methylsulphonylbenzoyl)-1,3-cyclohexanedione, 4,4-dimethyl-2-(4-methanesulphonyl-2-nitrobenzoyl)-1,3-cyclohexanedione, 2-(2-chloro-3-ethoxy-4-methanesulphonylbenzoyl)-5-methyl-1,3-cyclohexanedione, and 2-(2-chloro-3-ethoxy-4-ethanesulphonylbenzoyl)-5-methyl-1,3-cyclohexanedione.

[0015] Chloracetamide herbicides, also known as chloracetanilide herbicides, that may be used in the formulations described herein have the general formula



where R¹ and R² are each hydrogen or an alkyl group, and R³, and R⁴ are each hydrogen, an alkyl group, an alkenyl group, an alkoxy group, a carboxyl group, a cyclic group, a heterocyclic group, an aromatic group, a heteroaromatic group, or an alkynyl group. Examples include alachlor, acetochlor, metolachlor, s-metolachlor, propachlor, and butachlor.

[0016] The compositions described herein may also include various adjuvants and/or functional components such as activators, spreaders, safeners, wetters, stickers, builders, extenders, emulsifiers, dispersants, suspension agents, nutrients, fertilizers, compatibility agents, retardants, buffers, penetrants, and translocators. Other active ingredients may also be included to the extent they are

soluble in the solvents described herein and chemically compatible with other components. Concentrations of active ingredients in the solvents described herein may need adjusting to maintain a single-phase emulsifiable concentrate solution in the event other agents are added to the mixture.

[0017] The compositions described herein include a solution of at least about 2.5 wt% of an HPPD inhibitor herbicide dissolved in an agriculturally acceptable solvent. An agriculturally acceptable solvent is a solvent that is accepted for agricultural use by the U.S. Environmental Protection Agency, or is otherwise suitable for agricultural use. Propylene carbonate is accepted by the EPA. The other organic carbonates and other ketone solvents described herein are otherwise generally suitable for agricultural use.

[0018] The solution of HPPD inhibitor herbicide may be used alone, or additional active ingredients may be added. The anilide herbicides described above may be used, and other active ingredients may be used as well. The additional active ingredients may be dissolved in the solution or included as a suspension or emulsion with the solution. A second HPPD inhibitor herbicide may be included, either dissolved in the solution or as a suspension or emulsion, to provide enhanced effectiveness.

[0019] Any herbicides soluble in the carbonyl-containing solvents described above may be used in a blend with the HPPD inhibitor herbicides listed above. Anilide herbicides useful for blending with HPPD inhibitor herbicides in an agriculturally useful composition include metolachlor, acetachlor. Two example formulations of emulsifiable concentrates featuring blends of metolachlor and mesotrione are as follows:

Example 1

Component	Weight Percent
Metolachlor, technical	37

Mesotrione, technical	3.7
Propylene carbonate	49.07
Nansa [®] EVM 70/2E	6.6
Termul [®] 5500	3.85
Surfonic [®] L24-22	0.55

Example 2

Component	Weight Percent
Metolachlor, technical	37
Mesotrione, technical	3.7
Butylene carbonate	49.07
Nansa [®] EVM 70/2E	6.6
Termul [®] 5500	3.85
Surfonic [®] L24-22	0.55

In the examples above, Nansa[®] EVM 70/2E is a calcium dodecylbenzenesulfonate surfactant dissolved in propylene glycol and 2-ethylhexanol, available from Huntsman, LLC, Termul[®] 5500 is a butyl-initiated EO/PO block polymer available from Huntsman, LLC, and Surfonic[®] L24-22 is a nonionic alcohol ethoxylate surfactant available from Huntsman, LLC.

[0020] Other examples are as follows:

Example 3

Component	Weight Percent
Mesotrione, technical	10
Propylene carbonate	81
Emulsifier Blend	9

Example 4

Component	Weight Percent
Mesotrione, technical	4
Metolachlor, technical	40
Propylene carbonate	47
Emulsifier Blend	9

Example 5

Component	Weight Percent
Mesotrione, technical	5
Propylene carbonate	41
JEFFSOL [®] AG1732	45
Emulsifier Blend	9

Example 6

Component	Weight Percent
Mesotrione, technical	3.7
Metolachlor, technical	37
Propylene carbonate	25
JEFFSOL [®] AG1732	25.3
Emulsifier Blend	9

Example 7

Component	Weight Percent
Mesotrione, technical	6
Propylene carbonate	45
Acetophenone	40
Emulsifier Blend	9

Example 8

Component	Weight Percent
Mesotrione, technical	4
Metolachlor, technical	40
Propylene carbonate	25
JEFFSOL [®] AG1740	22
Emulsifier Blend	9

Example 9

Component	Weight Percent
Mesotrione, technical	3.8
Acetochlor, technical	38
Butylene carbonate	30
Aromatic 150	19.2
Emulsifier Blend	9

Example 10

Component	Weight Percent
Mesotrione, technical	3.8
Metolachlor, technical	38
Benoxacor (safener)	1.8
Butylene carbonate	24
JEFFSOL [®] AG1730	23.4
Emulsifier Blend	9

[0021] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

Claims:

1. A composition, comprising:
a solution of at least 2.5 wt% of an HPPD inhibitor herbicide dissolved in an agriculturally acceptable solvent that is stable at ambient conditions.
2. The composition of claim 1, wherein the HPPD inhibitor herbicide is mesotrione.
3. The composition of claim 1, wherein the agriculturally acceptable solvent is a carbonyl containing solvent.
4. The composition of claim 3, wherein the carbonyl containing solvent is an organic carbonate.
5. The composition of claim 1, further comprising a second active ingredient.
6. The composition of claim 5, wherein the second active ingredient is an anilide herbicide.
7. The composition of claim 6, wherein the HPPD inhibitor herbicide is mesotrione.
8. The composition of claim 7, wherein the anilide herbicide is metolachlor, s-metolachlor, or acetochlor.
9. The composition of claim 8, wherein the agriculturally acceptable solvent is a carbonyl containing solvent.

10. The composition of claim 5, wherein the agriculturally acceptable solvent is an organic carbonate.
11. The composition of claim 5, wherein the agriculturally acceptable solvent comprises a compound selected from the group consisting of propylene carbonate and butylene carbonate.
12. The composition of claim 11, further comprising a co-solvent.
13. The composition of claim 12, wherein the co-solvent is immiscible in water.
14. The composition of claim 11, wherein the composition is stable for at least 6 months.
15. An emulsifiable concentrate herbicide composition, comprising:
 - an HPPD inhibitor herbicide;
 - a chloranilide herbicide;
 - an alkylene carbonate; and
 - a water immiscible co-solvent.
16. The composition of claim 15, wherein the HPPD inhibitor herbicide is mesotrione.
17. The composition of claim 15, wherein the chloranilide herbicide is metolachlor, s-metolachlor, or acetochlor.
18. The composition of claim 15, wherein the alkylene carbonate comprises a compound selected from the group consisting of propylene carbonate and butylene carbonate.

19. The composition of claim 15, wherein the co-solvent is selected from the group consisting of cyclohexanone, acetophenone, a fatty acid dimethyl amide, a fatty acid morpholine amide, or a combination thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/53578

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A01N 63/00 (2013.01)

USPC - 504/118, 128, 148

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)
USPC-504/118Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC -504/128, 148 (see search terms below)

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

PatBase, PubWest, ProQuest Dialog, Google Scholar, Google Web

Search Terms: HPPD inhibitor, chloranilide, anilide, chloroacetanilide, chloroacetamide, herbicide, mesotrione, emulsifiable, solvent, carbonate, alkyiene, propylene, butylene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/0305953 A1 (Schnabel et al.) 11 December 2008 (11.12.2008) para [0008]-[0009], [0013], [0024], [0061], [0069], [0092], [0094], [0108],	1-19
X	US 2011/0053775 A1 (Dunne et al.) 03 March 2011 (03.03.2011) para [0005], [0008], [0032], [0041],	1-14
A	US 2011/0143938 A1 (Fowler et al.) 16 June 2011 (16.06.2011) para [0011], [0042], [0059],	15-19
A	US 2011/0065579 A1 (Sievernich et al.) 17 March 2011 (17.03.2011) abstract, [0299], [0357]	1-2, 7-8

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11 December 2013 (11.12.2013)

Date of mailing of the international search report

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