



(51) International Patent Classification:
A01N 25/30 (2006.01)

(21) International Application Number:
PCT/US2012/032265

(22) International Filing Date:
5 April 2012 (05.04.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/477,251 20 April 2011 (20.04.2011) US

(71) Applicant (for all designated States except US): **HUNTS-
MAN PETROCHEMICAL LLC** [US/US]; 10003 Wood-
loch Forest Drive, The Woodlands, TX 77380 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ELSIK, Curtis M.**
[US/US]; 42 North Terrace Mill Circle, The Woodlands,
TX 77382 (US).

(74) Agent: **KOROMPAI, Edward D.**; Hunstman Internation-
al LLC, Legal Department, 10003 Woodloch Forest Drive,
The Woodlands, TX 77380 (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, MD, 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).

Published:

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

(54) Title: SPRAY DRIFT REDUCTION AGENTS COMPRISING LOW HYDROPHILIC-LIOPHILIC BALANCE SURFACT-
ANTS

(57) Abstract: Embodiments of the present invention disclose using low hydrophilic-lipophilic balance surfactants as spray drift re-
duction agents and methods of using such agents. Such surf act ants generally reduce the amount of fines generated during spraying.
Rather, other surfactants usually increase the amount of fines when added to the spray tank since the reduced tension makes it easier
for the spray drops to break up. A pesticidal composition to reduce spray drift that comprises one or more active ingredients and one
or more low hydrophilic-lipophilic balance (HLB) surfactants. In embodiments, the one or more active ingredients may be herbi-
cides, insecticides, fungicides or combinations thereof. Such herbicides may be water soluble herbicides or other herbicides such as
2,4-D esters. The one or more active ingredients may be glyphosate or one or more salts or esters thereof.



Spray Drift Reduction Agents Comprising Low Hydrophilic-Lipophilic Balance Surfactants

Field of Invention

[0001] This invention relates generally to drift reduction agents for use in agricultural applications, but may also be applied in other applications where it is beneficial to reduce off-target deposition.

Background

[0002] Spray drift may be defined as the physical movement of airborne spray particles through the air at the time of application or soon thereafter to any off-target site. In the agricultural context, formulations with greater spray drift characteristics are typically unfavorable because less of the formulation interacts with the target site. To counteract spray drift, drift reduction agents are typically added to the spray mixtures to reduce the amount of spray drift that occurs.

[0003] There are many drift reduction technology (DRT) tank mix adjuvants (TMA) currently on the market today. They can be lumped into broad categories based on their individual chemistries. There are natural polymers such as guar gum and other polysaccharides. There are synthetic polymers such as the polyacrylamides. These both function to increase extensional or kinematic viscosity, and this increased viscosity usually results in increased particle size and reduced fines. Reducing fines generally reduces spray drift. However, the polymer systems tend to increase the average particle size and broaden the particle size distribution (PSD). Bioefficacy can be adversely affected when mean particle size becomes too wide.

[0004] There are also oil products available that can be mineral or natural based, such as esterified seed oil. These oils produce either emulsions or invert emulsions that are thought

to function by preventing small drops from forming during spray generation due to the emulsion phase present.

[0005] Surfactants are typically added to many pesticidal spray solutions to increase bioefficacy. When a surfactant is added to a spray solution the surface tension and dynamic surface tensions may be reduced. It is thought that this reduction in surface tension makes it easier to generate smaller droplets. Adding a surfactant typically reduces the average particle size and more importantly generally increases the amount of fines generated during spraying. It is the finer particles that typically drift the most. Therefore, despite their other benefits, surfactants are not typically thought of as agents to reduce spray drift.

Detailed Description of Invention

[0006] Surprisingly, it has been discovered that relatively low hydrophilic-lipophilic balance (HLB) surfactants may be used as spray drift reduction agents. Such surfactants generally reduce the amount of fines generated during spraying. Rather, other surfactants usually increase the amount of fines when added to the spray tank since the reduced tension makes it easier for the spray drops to break up.

[0007] Surfactants are amphiphilic molecules that concentrate at the interface between two phases and modify the properties of that interface. A list of surfactants can be found in McCutcheon's Emulsifiers & Detergents or the Industrial Surfactants Handbook. The hydrophilic-lipophilic balance (HLB) of a surfactant is measured on an empirical scale developed by Griffin (W.C.Griffin, J. Cosmet. Chem., 1, 311, 1949). This scale ranges from 0 to 20, with 0 for a completely lipophilic molecule and 20 for a completely hydrophilic molecule. The function of surfactants can be generally described by their HLB number. Defoaming surfactants have an HLB range of 1-3. Water-in-oil emulsifiers have an HLB range of 3-6. Wetting agents have an HLB range of 7-9. Oil-in-water emulsifiers have an HLB range of 8-18. Detergents have an HLB range of 13-15. Solubilizers have an HLB range of 15-18.

[0008] Surfactants with low HLB are not considered soluble in water. They are considered dispersible in water. They may form this dispersed phase spontaneously,

without agitation. In other words, low HLB surfactants form a surfactant-rich dispersed phase when added to water. The presence of the dispersed surfactant-rich phase is thought to reduce the amount of fines formed during the spray atomization process. This novel DRT TMA chemistry is not believed to deleteriously broaden the particle size distribution as the polymeric DRT agents do.

[0009] For this application, “low HLB” is defined as any surfactant HLB that will result in the surfactant’s cloud point as measured in the targeted spray system being below the temperature at which the system is sprayed. In some embodiments this HLB is from about 7 to about 9. However, the actual HLB required will therefore be a function of the spray system components and their concentrations. When spraying at temperatures above the surfactant cloud point, a dispersed surfactant-rich phase will form, and this dispersed phase will function to reduce the fines generated even though the surface tension is reduced due to the presence of the dispersed surfactant phase. Higher HLB surfactants should also reduce fines if used above their cloud point. This would normally require elevated temperatures in the absence of formulation additives designed to reduce the cloud point.

[0010] Examples of the low HLB surfactants of the current invention may include, but are not limited to, alcohol alkoxylates, alkylamine alkoxylates, polyetheramine alkoxylates, ethylene oxide/propylene oxide block polymers, phosphate esters, alkyl sulfates, alkyl ether sulfates, alkyl and alkylbenzene sulfonates, fatty acid esters, fatty oil alkoxylates, saccharide derivatives, sorbitan derivatives, alkyl phenol alkoxylates, arylphenol alkoxylates, sulphosuccinates and sulphosuccinamates and combinations thereof. The surfactants can be nonionic, anionic, cationic or zwitterionic.

[0011] Commercial examples of such low HLB surfactants include the SURFONIC® surfactants that are commercially available from the Huntsman Corporation of The Woodlands, Texas. SURFONIC® L12-3 surfactant is a linear C10-12 alcohol ethoxylate with an average 3 moles ethylene oxide (EO) and an HLB = 9.0. SURFONIC® L24-3 surfactant is a linear C12-16 alcohol ethoxylate with an average 3 moles ethylene oxide (EO) and an HLB = 8.0. SURFONIC® TDA-3B surfactant is a branched C13 alcohol ethoxylate with an average 3 moles ethylene oxide (EO) and an HLB = 8.0. SURFONIC® DA-4 surfactant is a branched C10 alcohol ethoxylate with an average 4 moles ethylene oxide (EO) and an HLB = 10.5. SURFONIC® CO-15 surfactant is a castor oil ethoxylate

with an average 15 moles ethylene oxide (EO) and an HLB = 8.2. SURFONIC® N-60 surfactant is a nonylphenol ethoxylate with an average of 6 moles EO and an HLB = 10.9. SURFONIC® T-5 surfactant is a tallowamine ethoxylate with an average of 5 moles EO and an HLB = 9.0.

[0012] Embodiments of the present invention also disclose a pesticidal composition to reduce spray drift that comprises one or more active ingredients and one or more low hydrophilic-lipophilic balance surfactants. In embodiments, the one or more active ingredients may be herbicides, insecticides, fungicides or combinations thereof. Such herbicides may be water soluble herbicides or other herbicides such as 2,4-D esters. In another embodiment, the one or more active ingredients may be glyphosate or one or more salts or esters thereof.

[0013] Embodiments of the present invention disclose a method of reducing spray drift by providing a composition for spraying that comprises a pesticide and a low hydrophilic-lipophilic balance surfactant and spraying the composition.

[0014] Further embodiments include a method of controlling weeds by contacting such a pesticidal composition to the weed or soil; a method of controlling insects by applying such a pesticidal composition to insects, soils or crops; and a method of controlling fungi by applying such a pesticidal composition to the fungi, crops or soils.

[0015] Embodiments of the present invention disclose a method of reducing spray drift comprising providing a composition for spraying that comprises a surfactant and spraying the spray mixture above the surfactant's cloud point as measured in the spray mixture.

[0016] Embodiments of the present invention disclose a spray composition comprising a blend of two or more surfactants wherein the blend has a low hydrophilic-lipophilic balance.

[0017] In other embodiments of the present invention, a method is disclosed of producing a spray drift reduction composition by blending a low HLB surfactant with a second surfactant (such as higher HLB surfactants) to produce a blend with a low hydrophilic-lipophilic balance. In order to counteract the usual deleterious spray drift effects of higher HLB surfactants, a user may add low HLB surfactants to a spray tank mixture. Here the pesticidal composition would have a blend of two or more surfactants where the effective surfactant blend has a combined low HLB level.

[0018] The primary application of this technology will be to reduce drift during the spraying of pesticide formulations. However, the technology may also be applicable in other areas such as polyurethane or polyurea spraying, paint spraying, or other spraying systems where it is beneficial to reduce off-target deposition.

[0019] To further illustrate various illustrative embodiments of the present invention, the following examples are provided.

Examples

[0020] Table 1 shows particle size data. The spray particle size distribution and percent fines can be measured using ASTM Standard Test Method E2798: "Characterization of Performance of Pesticide Spray Drift Reduction Adjuvants for Ground Application." Sample solutions were sprayed through a nozzle (XR8004VS) at 40 psig.

[0021] Example 1, the pesticide composition, contains 1.7v/v% POWERMAX® herbicide (commercially available from The Monsanto Company of St. Louis, Missouri. POWERMAX is a registered mark of The Monsanto Company) diluted into 342 ppm hardness water. Example 2 is the same base composition as Example 1 except it also contains 0.5v/v% SURFONIC® L24-3 surfactant which is commercially available from Huntsman Corporation of The Woodlands, Texas. SURFONIC® L24-3 surfactant is a linear C12-16 alcohol ethoxylate with an average 3 moles ethylene oxide (EO) and an HLB = 8.0. Example 3 is the same base composition as Example 1 except it also contains 0.5% SURFONIC® L12-3 surfactant which is commercially available from the Huntsman Corporation of The Woodlands, Texas. SURFONIC L12-3 surfactant is a linear C10-12 alcohol ethoxylate with an average 3 moles ethylene oxide (EO) and an HLB = 9.0. Example 4 is the same base composition as Example 1 except it also contains 0.5% SURFONIC® TDA-3B surfactant which is commercially available from Huntsman Corporation of The Woodlands, Texas. SURFONIC TDA-3B surfactant is a branched C13 alcohol ethoxylate with an average 3 moles ethylene oxide (EO) and an HLB = 8.0. Example 5 is the same base composition as Example 1 except it also contains 0.5% TERMIX® 5910 tank mix adjuvant which is commercially available from Huntsman Corporation of The Woodlands, Texas.

Table 1: Particle Size Data

Example	%FINE S <105 μm	D10 (μm)	VMD [D50] (μm)	D90 (μm)	REL SPAN	KINE VISC (cSt)	DST @ 10mS (mN/m)	DST @ 1s (mN/m)	EXT VISC
1	16.0	85.7	198.6	387.9	1.52	0.734	51.3	42.9	1.00
2	10.8	100.0	265.4	420.9	1.21	0.844	52.5	32.1	6.94
3	9.4	107.5	238.2	404.6	1.25	0.870	36.6	27.5	6.93
4	8.7	112.5	273.4	426.7	1.15	0.827	48.8	26.9	6.84
5	9.8	105.8	251.8	412.5	1.22	0.743	43.4	29.7	6.80

[0022] Table 1 shows several low HLB surfactants that reduce the amount of fines while also reducing both dynamic (10 mSec) and static (1 s) surface tension. Table 1 also shows that the low HLB surfactant SURFONIC TDA-3B reduced %fines < 105 microns from 16.0 v/v% with no DRT adjuvant to a value of only 8.7 %. This is almost a 50% reduction in fines, while dynamic surface tension dropped from 51.3 to 48.8 mN/m and static surface tension dropped from 42.9 to 26.9 mN/m. Normally a reduction in tension would result in an increase in the volume of fines generated during spraying.

[0023] Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations may be made herein without departing from the spirit and scope of the invention as defined by the appended claims.

Claims:

- 1) A spray drift reduction agent comprising a low hydrophilic-lipophilic balance surfactant.
- 2) A pesticidal composition to reduce spray drift that comprises one or more active ingredients and one or more low hydrophilic-lipophilic balance surfactants.
- 3) A composition of claim 2 wherein the one or more active ingredients comprise a herbicide.
- 4) A composition of claim 2 wherein the one or more active ingredients comprise an insecticide.
- 5) A composition of claim 2 wherein the one or more active ingredients comprise a fungicide.
- 6) A method of reducing spray drift comprising providing a composition for spraying that comprises a pesticide and a low hydrophilic-lipophilic balance surfactant and spraying the composition.
- 7) A method of reducing spray drift comprising:
 - adding a surfactant to a spray mixture; and,
 - spraying the spray mixture at a temperature above the surfactant's cloud point as measured in the spray mixture.
- 8) A spray composition comprising a blend of two or more surfactants wherein the blend has a low hydrophilic-lipophilic balance.

- 9) A method of producing a spray drift reduction composition comprising blending a low hydrophilic-lipophilic balance surfactant with a second surfactant to produce a blend with a low hydrophilic-lipophilic balance.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/32265

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A01N 25/30 (2012.01)

USPC - 504/358

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8)- A01N 25/30 (2012.01);

USPC- 504/358

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: spray, drift, hydrophilic, lipophilic, balance, HLB, pesticide, herbicide, insecticide, fungicide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/0191026 A1 (KILLICK et al.) 9 October 2003 (9.10.2003), para [0015], [0017], [0023], [0028], [0035], [0036], [0039], [0042], [0043], [0050], [0064]	1-6, 8, 9
Y	US 2006/0270556 A1 (WRIGHT et al.) 30 November 2006 (30.11.2006), para [0013], [0016], [0020], [0041], [0047], [0049], [0070]-[0072], [0098], [0099], [0139], [0146]	7
Y	US 2006/0154826 A1 (BERNARDINI et al.) 13 July 2006 (13.07.2006), para [0010]-[0020], [0042], [0048], [0050]	7
Y	US 2008/0020933 A1 (TANN et al.) 24 January 2008 (24.01.2008), para [0008]-[0060]	1-9
Y	WO 03/096807 A1 (ELSIK et al.) 27 November 2003 (27.11.2003), pg 8-93	1-9

☐ 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

25 June 2012 (25.06.2012)

Date of mailing of the international search report

18 JUL 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