

SILOXANE NONIONIC BLENDS USEFUL IN AGRICULTURE

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Many pesticides require the addition of an
adjuvant to the spray mixture to provide wetting and
spreading on foliar surfaces. Often that adjuvant is
5 a surfactant which can perform a variety of functions,
such as increasing spray droplet retention on
difficult to wet leaf surfaces, or to provide
penetration of the herbicide into the plant cuticle.
These adjuvants are either provided as a component in
10 an adjuvant formulation or used as an additive in
herbicide formulations.

Trisiloxane alkoxyates are well known for
their ability to provide enhanced spreading and
wetting properties to pesticide spray solutions,
15 relative to more commonly used organic based
(nonsilicone) surfactants. At times it is necessary
to include other surfactants in the spray mixture
along with the trisiloxane alkoxyate. Unfortunately,
the presence of many classes of cosurfactants
20 interfere with the performance of the trisiloxane
alkoxyate.

The present invention teaches a surfactant
composition of nonionic siloxane alkoxyates and
aminoalkyleneoxide surfactant, and their use as
25 adjuvants, for pesticides. The present invention
provides a surfactant composition that gives enhanced
wetting of spray solutions on difficult to wet
surfaces, such as waxy plants, and enhance the uptake
of agrichemicals into plants as compared to more

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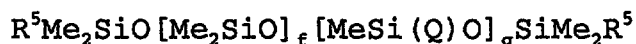
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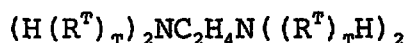
1 commonly used blends of polyalkyleneoxide/trisiloxane
alkoxylate surfactants.

The composition of the present invention is
useful as a tank side additive, or as a component in a
5 herbicide formulation. In addition, the compositions
of the present invention are useful as adjuvants for
other pesticides, such as fungicides, insecticides,
plant growth regulators, acaricides and the like.

More specifically, the present invention is
10 directed to a composition comprising (a) a nonionic
siloxane of the formula:



wherein $f=0$ to 1 , $g=1$ to 2 , $Q=C_dH_{2d}O(C_2H_4O)_t(C_3H_6O)_wR^4$,
 $d=2$ to 4 , $t=3$ to 12 , $w=0$ to 8 , R^4 is hydrogen, acetyl
15 or a hydrocarbon radical containing 1 to 4 carbon
atoms, and R^5 is Q , alkyl of one to four carbons or a
hydroxyl group; and (b) an aminopolyalkyleneoxide of
the formula



20 wherein R^T denotes alkoxy groups containing 2 or 3
carbon atoms each, and the subscript T is selected so
that the molecular weight of the alkoxylated diamine
is 1,000 to 15,000.

The present invention provides novel
25 surfactant compositions that are useful as adjuvants
for pesticides. The compositions of the present
invention provide enhanced spray coverage relative to
conventional wetting agents. In addition, these
products provide a low aqueous surface tension (<23

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- 1 mN/m at 0.1 wt%), which is necessary and desirable for spreading of pesticide solutions.

COMPOSITION

- The compositions of the present invention include a nonionic siloxane alkyloxyate and an aminopolyalkyleneoxide.

a. Nonionic siloxane alkoxyate

The siloxane alkoxyate has the general formula:

- 10 $R^5Me_2SiO[Me_2SiO]_f[MeSi(Q)O]_gSiMe_2R^5$
wherein $f=0$ to 1, preferably 0, $g=1$ to 2, preferably 1, $Q = C_dH_{2d}O(C_2H_4O)_t(C_3H_6O)_wR^4$, $d = 2$ to 4, preferably 3, $t=3$ to 12, preferably 4 to 8, $w = 0$ to 8, providing that when w is >0 , $(t+w)$ is preferably between 5 and
15 12. R^4 is hydrogen, acetyl or a hydrocarbon radical between 1 and 4 carbon atoms. R^5 is Q , alkyl of one to four carbons or a hydroxyl group. The preferred nonionic siloxane alkoxyates are trisiloxane alkoxyates, which have $f = 0$, $g = 1$, $d = 3$, $t = 4$ to
20 8, $w = 0$, R^4 is H or Me.

b. Aminopolyalkyleneoxide

- The compositions of the present invention also contain aminopolyalkyleneoxide surfactants which do not detract from the efficacy of the composition.
25 Examples include alkoxyated diamines of the formula $(H(R^T)_T)_2NC_2H_4N((R^T)_TH)_2$ wherein R^T denotes alkoxy groups containing 2 or 3 carbon atoms each, and the subscript T is selected so that the molecular weight of the alkoxyated diamine is 1,000 to 15,000. Preferably,

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1 ethoxy units comprise 10 to 90% and more preferably 20
to 50% of the polyalkoxylate chains.

The ratio of the aminopolyalkyleneoxide to
the nonionic siloxane alkoxylate is in the range of
5 99:1 and 1:99 by weight.

The compositions of the present invention
also optionally include ingredients for use herein
which are pesticides, especially acid functional ones,
e.g., compounds that contain at least one carboxylic,
10 sulfonic or phosphonic acid group which is in the form
of the free acid or a salt or ester thereof. The term
pesticide means any compound used to destroy pests,
e.g., insecticides, rodenticides, fungicides, and
herbicides, and is also used herein to include plant
15 growth regulatory compounds. Illustrative examples of
pesticides which can be employed include, but are not
limited to, growth regulators, photosynthesis
inhibitors, pigment inhibitors, mitotic disrupters,
lipid biosynthesis inhibitors, cell wall inhibitors,
20 and cell membrane disrupters. The amount of pesticide
employed in compositions of the invention varies with
the type of pesticide employed. More specific
examples of pesticide compounds that can be used with
the compositions of the invention are: phenoxy acetic
25 acids, phenoxy propionic acids, phenoxy butyric acids,
benzoic acids, triazines and s-triazines, substituted
ureas, uracils, bentazon, desmedipham, methazole,
phenmedipham, pyridate, amitrole, clomazone,
fluridone, norflurazone, dinitroanilines, isopropalin,
30 oryzalin, pendimethalin, prodiamine, triflualin,

1 glyphosate, sulfonylureas, imidazolinones,
cyclohexanediones, aryloxyphenoxypropanoates,
dichlobenil, isoxaben, and bipyridylium compounds.

MANUFACTURE

5 The nonionic siloxane alkoxylates,
aminoalkyleneoxide surfactants, and pesticides are
commercially available and their manufacture is known
in the art.

USE

10 The nonionic siloxane alkoxylates,
aminoalkyleneoxide surfactant blends of the present
invention, primarily are intended for use in the
agricultural field as adjuvants for pesticide,
especially acid functional pesticides, containing
15 aqueous end-use formulations. The compositions of the
present invention are added directly to a spray tank
along with an acid functional pesticide, or as part of
a pesticide formulation. They are used in an
effective amount, that is, an amount which is
20 sufficient to cause the pesticide to function
effectively in the formulation. When used as a
tankside additive, the compositions of this invention
should be present at weight concentrations between
0.01% and 5.0%, preferably between 0.025% and 0.5%,
25 but in "in can" formulations, the compositions of the
present invention may be present at concentrations
that will deliver between 0.01% and 5.0% to the final
use dilution, preferably between 0.025% and 0.5%, of
the final use dilution.

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1 The novel nonionic siloxane
alkoxylates/aminoalkyleneoxide surfactant compositions
of the present invention may also be used generally as
surface active agents in aqueous formulation where
5 there is an acid functionalized component, including,
but not limited to, surfactants, wetting agents and
softeners for textiles, as flowing and leveling agents
in coatings, in hair care products and creams for
personal care applications and as anti-static agents
10 and softeners for laundry products. Other uses for
the present composition will be obvious to those of
skill in the art.

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1 EXAMPLES

The following examples are presented to further illustrate and explain the present invention and should not be taken as limiting in any regard.

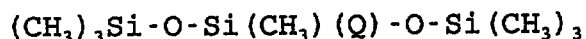
- 5 Unless otherwise indicated, all parts and percentages are by weight, and are based on the weight at the particular stage of the processing being described.

Example 1

10 The composition of the present invention contains at least one surfactant from the class of nonionic siloxane alkoxyates (a), and at least one surfactant from the class of aminoalkyleneoxide surfactants (b).

a. Nonionic Siloxane Alkoxyates:

15 Tables 1 and 2 describes the trisiloxane alkoxyates used herein as illustrative examples of the compositions of the present invention. They have the following structure:



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Table 1

Reference

Nominal Formula of the Z Group

TSA-1

$\text{C}_3\text{H}_6\text{O}(\text{C}_2\text{H}_4\text{O})_6\text{CH}_3$, Silwet L-77® Surfactant

25 TSA-2

$\text{C}_3\text{H}_6\text{O}(\text{C}_2\text{H}_4\text{O})_6\text{OH}$, Silwet® 408

b. Aminoalkyleneoxide Surfactants

Table 2 provides structural information on the aminoalkyleneoxide surfactants component of this instant invention. The aminopolyalkyleneoxide

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1 surfactants may be blocked, or random alkyleneoxide groups.

Table 2

5 **Description of Conventional Aminoalkyleneoxide Surfactants**

	<u>References</u>	<u>MW</u>	<u>Wt.%EO</u>	<u>Configuration of EO/PO</u>
	AAO-1	1,650	40	Terminal EO Block
	AAO-2	3,600	10	Terminal EO Block
	AAO-3	5,500	40	Terminal EO Block
	AAO-4	6,700	40	Terminal EO Block
10	AAO-5	25,000	80	Terminal EO Block
	AAO-6	30,000	80	Terminal EO Block
	AAO-7	4,580	10	Terminal EO Block

Comparative Nonsilicone Surfactants:

15 Table 3 provides descriptions of a typical, comparative, nonsilicone surfactant, used as an agricultural wetting agent.

Table 3

Description of Comparative Conventional Nonsilicone Surfactant

	<u>Ref.</u>	<u>MW</u>	<u>Wt%EO</u>	<u>Remarks</u>
20	PAO-A	2150	20	Pluronic® 17R2 (BASF Corp.), polyalkyleneoxide block copolymer surfactant (PO-EO-PO type).
25	PAO-B	2500	20	Pluronic® L-62 (BASF Corp.), polyalkyleneoxide block copolymer surfactant (EO-PO-EO type).
	OPE	NA	10	Octylphenol ethoxylate (TRITON® X-100) (Union Carbide Corp.)
30	TAE	NA	5	Tallow amine ethoxylate (ETHOMEEN® T/15) (Akzo Nobel)

1 Example 2 - Spreading:

 This example demonstrates that the
surfactant blend compositions of the present invention
are favorable in their ability to provide spreading
5 properties equivalent to the commonly used PAO-A/TSA-1
blends. Table 4 shows that although the
aminoalkyleneoxide surfactants are a unique class of
surfactants, these materials do not inhibit the
spreading properties of the TSA-1, when compared at
10 equivalent TSA-1 concentrations (compare ID 29-31 with
AAO/TSA-1 blends). Additionally, TSA-1 blends, with
either OPE or TAE, show a significant reduction in the
spreading properties as compared to the compositions
of the present invention (Compare ID 32,33 with
15 AAO/TSA-1 blends). Spreading was determined by
applying a 10 μ L droplet of surfactant solution to a
polyester film (3M, Write-On film) and measuring the
spread diameter after 30 seconds. The solution was
applied with an automatic pipette to provide droplets
20 of reproducible volume. Deionized water that was
further purified with a Millipore filtration system
was used to prepare the surfactant solutions.

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1 Table 4

Comparison of Spreading Properties^(a) (@0.1 wt%)
of TSA-1/Cosurfactant Blends

	ID	Cosurfactant	Composition of Invention	Wt% TSA-1	Wt% Cosurfactant	Spread Diameter (mm)
5	1	AAO-1	No	0	0.1	6
	2	AAO-1	Yes	0.025	0.075	22
	3	AAO-1	Yes	0.05	0.05	29
	4	AAO-1	Yes	0.075	0.025	39
	5	AAO-2	No	0	0.1	7
	6	AAO-2	Yes	0.025	0.075	19
	7	AAO-2	Yes	0.05	0.05	36
10	8	AAO-2	Yes	0.075	0.025	43
	9	AAO-4	No	0	0.1	6
	10	AAO-4	Yes	0.025	0.075	24
	11	AAO-4	Yes	0.05	0.05	35
	12	AAO-4	Yes	0.075	0.025	44
	13	AAO-5	No	0	0.1	6
	14	AAO-5	Yes	0.025	0.075	21
15	15	AAO-5	Yes	0.05	0.05	35
	16	AAO-5	Yes	0.075	0.025	45
	17	AAO-6	No	0	0.1	7
	18	AAO-6	Yes	0.025	0.075	22
	19	AAO-6	Yes	0.05	0.05	35
	20	AAO-6	Yes	0.075	0.025	43
	21	AAO-7	No	0	0.1	7
20	22	AAO-7	Yes	0.025	0.075	29
	23	AAO-7	Yes	0.05	0.05	40
	24	AAO-7	Yes	0.075	0.025	52
	25	PAO-A	No	0	0.1	7
	26	PAO-A	No	0.025	0.075	27
	27	PAO-A	No	0.05	0.05	35
	28	PAO-A	No	0.075	0.025	45
25	29	None	N/A	0.025	0	20
	30	None	N/A	0.050	0	31
	31	None	N/A	0.075	0	40
	32	OPE	No	0.05	0.05	20
	33	TAE	No	0.05	0.05	8
	34	None	N/A	0	0	4

a. Spreading of 0.1 wt% solution on polyester film.

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1 Example 3

The effect of adjuvant on glyphosate efficacy was determined using a barley regrowth assay. Glyphosate treatments, with and without adjuvant, were sprayed on
5 barley (14-16 cm tall) at rates of 0.125, 0.25 and 0.5 lbs ae/acre. Six hours after application, all plants were trimmed to 2 cm in height, removing 95% of the treated area. Regrowth was assessed 1 week after treatment by measuring
10 fresh weight and plant height. The data are reported as percent inhibition as compared to the untreated control.

Table 5 demonstrates that overall the compositions of the present invention (AAO/TSA-2 combinations) provide enhanced glyphosate efficacy relative to the PAO-B/TSA-2 blend, or as compared to glyphosate without surfactant.

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Table 5

Summary of Surfactant Effects on Glyphosate Activity

	<u>ID</u>	<u>Surfactant</u>	<u>Composition of Invention</u>	<u>Glyphosate lb ae/acre</u>	<u>% Inhibition Fresh Wt.</u>
20	22	AAO-1/TSA-2	Yes	0.5	57.2
	23	AAO-1/TSA-2	Yes	0.25	23.2
	24	AAO-1/TSA-2	Yes	0.175	14.4
	32	AAO-2/TSA-2	Yes	0.5	70.3
	33	AAO-2/TSA-2	Yes	0.25	52.5
	34	AAO-2/TSA-2	Yes	0.175	2.6
	35	AAO-3/TSA-2	Yes	0.5	72.5
25	36	AAO-3/TSA-2	Yes	0.25	25.2
	37	AAO-3/TSA-2	Yes	0.175	12.2
	38	AAO-7/TSA-2	Yes	0.5	79.4
	39	AAO-7/TSA-2	Yes	0.25	41.8
	40	AAO-7/TSA-2	Yes	0.175	10.3
	41	PAO-B/TSA-2	No	0.5	49.8
	42	PAO-B/TSA-2	No	0.25	43.8
30	43	PAO-B/TSA-2	No	0.125	21.4

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1	44	None	N/A	0.5	39.7
	45	None	N/A	0.25	20.2
	46	None	N/A	0.125	0.6

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1 I Claim:

1. A composition comprising

a. a nonionic siloxane of the formula:

5 $R^5Me_2SiO[Me_2SiO]_f[MeSi(Q)O]_gSiMe_2R^5$

wherein $f=0$ to 1 , $g=1$ to 2 , $Q=C_dH_{2d}O(C_2H_4O)_t(C_3H_6O)_wR^4$, $d=2$ to 4 , $t=3$ to 12 , $w=0$ to 8 , R^4 is hydrogen, acetyl or a hydrocarbon radical containing 1 to 4 carbon atoms, and R^5 is Q , alkyl of one to four carbons or a hydroxyl group; and

10 b. an aminopolyalkyleneoxide of the formula



wherein R^T denotes alkoxy groups containing 2 or 3 carbon atoms each, and the subscript T is selected so that the molecular weight of the alkoxylated diamine is $1,000$ to
15 $15,000$.

2. A composition according to claim 1 wherein the weight ratio of component a. to component b. is $1:99$ to $99:1$.

20 3. A composition according to claim 1 additionally comprising an acid functional pesticide.

4. A composition according to claim 3 where the acid functional pesticide is selected from: growth regulators,
25 photosynthesis inhibitors, pigment inhibitors, mitotic disrupters, lipid biosynthesis inhibitors, cell wall inhibitors, and cell membrane disrupters.

5. A composition according to claim 3 wherein the pesticide
30 is a herbicide selected from the group consisting of:



- 1 phenoxy acetic acids, phenoxy propionic acids, phenoxy
butyric acids, benzoic acids, triazines and s-triazines,
substituted ureas, uracils, bentazon, desmedipham,
methazole, phenmedipham, pyridate, amitrole, clomazone,
5 fluridchlorflurazone, dinitrioanilines, isopropalin,
oryzalin, pendimethalin, prodiamine, trifluralin,
glyphosate, glufosinate, sulfonylureas, imidazolinones,
clethodim, diclofop-methyl, fenoxaprop-ethyl, fluazifop-p-
butyl, haloxyfop-methyl, quizalofop, sethoxydim,
10 dichlobenil, isoxaben, and bipyridylium compounds.

6. A process for treating plants comprising applying to
plants an effective amount of a composition according to
claim 1.

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7. A process for treating plants comprising applying to
plants an effective amount of a composition according to
claim 2.

20 8. A process for treating plants comprising applying to
plants an effective amount of a composition according to
claim 3.

9. A process for treating plants comprising applying to
25 plants an effective amount of a composition according to
claim 4.

10. A process for treating plants comprising applying to
plants an effective amount of a composition according to
30 claim 5.