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WEB SITE: www.cavelier-abogados.com
E-MAIL: cavelier@colomsat.net.co

EDIFICIO SISKI
CARRERA 4 No. 72 - 35
BOGOTÁ 8, COLOMBIA

Superintendencia de Industria y Comercio
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Señora Jefe de la
DIVISION DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
E. S. D.

Referencia : Expediente No. 00.029.094
Solicitante : MONSANTO COMPANY
Asunto : Solicitud de patente para: "MÉTODO PARA
MEJORAR LA EFECTIVIDAD BIOLÓGICA DE
COMPOSICIONES PARA TRATAMIENTO DE PLANTAS"
Fecha de solicitud : 19 de abril de 2000

TRAMITE: 002 - EVENTO: 001 - ACTUACION: 329

1. Yo, Emilio FERRERO, obrando como apoderado de la solicitud en referencia, atentamente presento con este escrito la copia certificada de la solicitud de patente estadounidense No. 60/130.756 del 23 de abril de 1999, junto con la traducción de sus reivindicaciones y certificaciones de la cual se reclama prioridad en esta solicitud de patente.

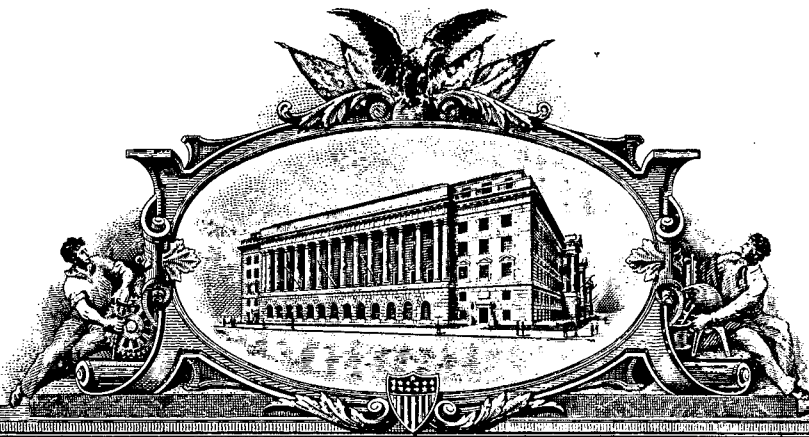
2. Ruego a la Señora Jefe se sirva aceptar este escrito con sus anexos, y se continúe con el trámite de la solicitud.

Bogotá, 18 JUL. 2000
Señora Jefe,


EMILIO FERRERO
T.P.A. No. 31.929

COLO 01759-801-001-9

lllR MRE-15



THE UNITED STATES OF AMERICA

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UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

April 11, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/130,756 ✓

FILING DATE: April 23, 1999



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

**P. SWAIN
Certifying Officer**

A/PROV 158 101

PTO/SB/16(6-95)

Approved for use through 04/11/98. OMB 0651-0037
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PROVISIONAL APPLICATION COVER SHEET

is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(c).

Docket Number	39-21(3755)A	Type a plus sign (+) inside this box	
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INVENTOR(s)/APPLICANT(s)

LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
Brinker	Ronald	J.	Ellisville, Missouri
Dyszlewski	Andrew	D.	Maryland Heights, Missouri
Gillespie	Jane	L.	St. Louis, Missouri
Jones	Claude	R.	St. Louis, Missouri
Kramer	Richard	M.	Chesterfield, Missouri
Pallas	Norman	R.	St. Louis, Missouri
Radke	Rodney	O.	St. Charles, Missouri
Ward	Anthony	J.I.	St. Louis, Missouri
Xu	Xiaodong	C.	St. Louis, Missouri

TITLE OF THE INVENTION (280 characters max)

METHOD OF ENHANCING BIOLOGICAL EFFECTIVENESS OF PLANT TREATMENT COMPOSITIONS

CORRESPONDENCE ADDRESS

Gail Wuellner
MONSANTO COMPANY - M2A
800 North Lindbergh Boulevard
Saint Louis

STATE	Missouri	ZIP CODE	63167	COUNTRY	USA
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ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification	Number of Pages	109	☐ Small Entity Statement
☒ Drawing(s)	Number of Sheets	1	Other (specify)

METHOD OF PAYMENT (check one)

☐ A check or money order is enclosed to cover the Provisional filing fees		PROVISIONAL FILING FEE AMOUNT(S)	
☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number:	13-4125		\$150.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.
☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,

SIGNATURE

James C. Forbes

Date

April 23, 1999

TYPED or PRINTED NAME

James C. Forbes

REGISTRATION NO.
(if appropriate)

39,457

☐	Additional inventors are being named on separately numbered sheets attached hereto.
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PROVISIONAL APPLICATION FILING ONLY

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PATENT
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PROVISIONAL PATENT APPLICATION

for

METHOD OF ENHANCING BIOLOGICAL EFFECTIVENESS OF
PLANT TREATMENT COMPOSITIONS

by

Ronald J. Brinker, Andrew D. Dyszlewski, Jane L. Gillespie, Claude R. Jones,
Richard M. Kramer, Norman R. Pallas, Rodney O. Radke, Anthony J. I. Ward
and Xiaodong C. Xu

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I hereby certify that this Patent Application is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. §1.10 on the date indicated above and is addressed to:	
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METHOD OF ENHANCING BIOLOGICAL EFFECTIVENESS OF
PLANT TREATMENT COMPOSITIONS

FIELD OF THE INVENTION

5 The field of the present invention is that of exogenous chemical substances applied to foliage of plants, and more particularly that of enhancing biological effectiveness of compositions of such exogenous chemical substances.

10 The term "exogenous chemical substance" as used herein means a chemical substance, whether naturally or synthetically obtained, which is applied to a plant to result in expressing a desired biological activity. The term "biological activity" as used herein means elicitation of a stimulatory, inhibitory, regulatory, therapeutic, toxic or lethal response in the plant or in a pathogen, parasite or feeding organism present in or on the plant. Examples of exogenous chemical substances include, but are not limited to, chemical pesticides (such as herbicides, algicides, fungicides, bactericides, viricides, insecticides, miticides, nematocides and molluscicides), plant growth
15 regulators, fertilizers and nutrients, gametocides, defoliants, desiccants, mixtures thereof and the like.

The term "biological effectiveness" is used herein to denote the degree to which a desired biological activity is expressed upon application of an exogenous chemical substance to foliage of a plant, or alternatively to denote the dosage or rate
20 of application of the exogenous chemical substance that results in the desired biological activity being expressed to a given degree. For example, where the exogenous chemical substance is a herbicide, biological effectiveness can be measured by the degree of inhibition of plant growth resulting from application of a particular rate of the herbicide, or by the application rate of the herbicide required to
25 cause a particular degree of inhibition, *e.g.*, 50% or 85% inhibition. Thus increased or enhanced biological effectiveness of a herbicide can be exhibited for example as an increased level of plant growth inhibition at a given rate of the herbicide, or as a reduction in the minimum rate of the herbicide giving a certain threshold level of plant growth inhibition.

30 BACKGROUND OF THE INVENTION

For many purposes in agriculture and related endeavors it is desired to treat

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plants with exogenous chemical substances of various kinds. Many exogenous chemical substances are applied to foliage (*i.e.*, leaves and other non-woody above-ground parts) of a plant, and have a site of action in the plant either close to or remote from the locus of application. Such substances are referred to herein as foliar-applied exogenous chemical substances.

Typically, when an exogenous chemical substance is applied to foliage by plant treatment processes known in the art, only a small portion of the amount applied reaches sites of action in the plant where a desired biological activity of the exogenous chemical substance can be usefully expressed. It is therefore a major desideratum in agriculture and related endeavors to enhance the efficiency of delivery of foliar-applied exogenous chemical substances to their sites of action in plants, and thereby to enhance the biological effectiveness of the exogenous chemical substance for the purpose for which the exogenous chemical substance is used.

Application to foliage of an exogenous chemical substance by processes known in the art does not universally result in inefficient delivery to sites of action. In some situations such processes provide excellent biological effectiveness, even at a low use rate of the exogenous chemical substance. In other situations the same processes, using the same rate of the same exogenous chemical substance, provide inadequate biological effectiveness. Thus, these processes are inconsistent in the result they provide, or they cannot be relied upon to provide the desired result.

A problem is that it is seldom possible to identify in advance those situations where good biological effectiveness will be obtained, partly because so many factors influence efficiency of delivery. These factors include weather (temperature, relative humidity, daylength, cloudiness, precipitation, wind, *etc.*) preceding, during and following application, soil conditions (fertility, aeration, *etc.*), plant growth stage, health and physiological status, equipment-related inaccuracies in application, and other factors. Therefore, to help ensure reliable or consistent biological effectiveness of a foliar-applied exogenous chemical substance, the user typically applies the substance at a higher rate than is truly necessary in the majority of situations.

Variability in biological effectiveness in field conditions is an especially troublesome problem in the case of exogenous chemical substances that are acids, and are typically formulated as water-soluble salts in which the exogenous chemical

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substance is present in an anionic form. Sometimes by converting such acid substances to esters, this variability can be moderated; however, in many cases esters show reduced biological effectiveness, for example due to inadequate conversion back to the parent acid once inside the treated plant. There remains a strong need for enhanced biological effectiveness, and enhanced reliability of biological effectiveness, of foliar-applied exogenous chemical substances, particularly anionic exogenous chemical substances.

The term "anionic exogenous chemical substance" as used herein means an exogenous chemical substance whose molecular structure includes one or more acid, or proton-donating, sites, and is therefore capable of forming an anion in the presence of a proton acceptor. The term therefore embraces substances that are zwitterionic. In describing an exogenous chemical substance as "anionic" herein, it is not implied that the exogenous chemical substance is necessarily in anionic form or that it is dissociated.

Benefits of a process providing greater reliability of biological effectiveness include an ability to reduce rates of application of exogenous chemical substances without sacrificing consistency of biological effectiveness. Pressures felt by the agricultural industry to reduce pesticide, particularly herbicide, usage are well evidenced by symposia on the subject, such as that held in 1993 by the Weed Science Society of America and documented in *Weed Technology* 8, 331-386 (1994). Reduced use rates bring rewards not only environmentally but also economically, as the cost per unit area treated decreases.

Foliar-applied exogenous chemical substances have frequently been applied together with amphiphilic materials, particularly amphiphilic surface-active agents, otherwise known as surfactants. Surfactants can influence biological effectiveness of a foliar-applied exogenous chemical substance in numerous ways.

When a dilute aqueous composition of an exogenous chemical substance is applied to foliage by conventional hydraulic spraying, the presence of surfactant in the dilute aqueous composition can alter the size distribution of the spray droplets, typically increasing the percentage of spray volume in the form of small droplets and reducing the percentage of spray volume in the form of large droplets. As smaller droplets have lower momentum than larger droplets, these smaller droplets are less

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likely to rebound from a foliar surface and consequently are more likely to be retained on that surface. Spray retention can also be facilitated by adhesion of surfactant molecules in a spray droplet to the foliar surface, which in most plants is waxy and hydrophobic. This adhesion reduces not only rebound but also run-off of spray droplets from the foliar surface. Surfactants also tend to increase the area of contact between a spray droplet and a foliar surface, and in many cases enhance penetration of an exogenous chemical substance from the droplet into and through cuticles of leaves to reach internal leaf tissues.

Through these and perhaps other effects, amphiphilic materials including surfactants have long been known to increase the biological effectiveness of exogenous chemical substances. It is therefore commonplace for one or more surfactants to be included in commercial formulations of foliar-applied exogenous chemical substances, even in formulations that do not require the presence of surfactants for acceptable physical stability or handling properties, for example as emulsifying or suspending agents or dispersants.

One of the most extensively studied of foliar-applied anionic exogenous chemical substances, from the point of view of the role of surfactants in enhancing biological effectiveness, is the herbicide glyphosate. As well as being a phytotoxic agent, glyphosate has been used as a plant growth regulator.

Glyphosate (N-phosphonomethylglycine) in its strict sense is an acid compound, but the word "glyphosate" is herein used in a less restrictive sense, except where the context dictates otherwise, to encompass not only glyphosate acid but also salts, adducts and esters thereof, and compounds which are converted to glyphosate in plant tissues or which otherwise provide glyphosate ions. In most commercial formulations of glyphosate, the glyphosate is present as a water-soluble salt. In this respect, glyphosate is typical of most exogenous chemical substances that are acids or that form anions.

Herbicidal salts of glyphosate are disclosed, for example, in U.S. Patent No. 3,799,758 to Franz, U.S. Patent No. 3,853,530 to Franz, U.S. Patent No. 4,140,513 to Prill, U.S. Patent No. 4,315,765 to Large, U.S. Patent No. 4,405,531 to Franz, U.S. Patent No. 4,481,026 to Prisbylla and U.S. Patent No. 4,507,250 to Bakel. Typical of such salts are alkali metal, for example sodium and potassium, salts; ammonium salt;

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and numerous salts having an ammonium, sulfonium or sulfoxonium cation substituted with 1-3 organic groups containing in total 1-6 carbon atoms, for example dimethylammonium, isopropylammonium, ethanolammonium and trimethylsulfonium salts.

- 5 Commercial formulations of glyphosate salts include, for example, Roundup®, Accord®, Roundup® Ultra and Roundup® Xtra herbicides of Monsanto Company, which contain the isopropylammonium salt, Roundup® Dry and Rival® herbicides of Monsanto Company, which contain the ammonium salt, Roundup® Geoforce herbicide of Monsanto Company, which contains the sodium salt, and Touchdown®
10 herbicide of Zeneca, which contains the trimethylsulfonium salt.

- Glyphosate as a herbicide has many advantages, particularly environmental advantages including biodegradability and low ecotoxicity. However, studies have shown that even the most biologically effective formulations of glyphosate presently in use do not deliver glyphosate efficiently to sites in the plant where the glyphosate
15 exerts its phytotoxic effect. Typically, only a small fraction of the applied herbicide arrives at such sites.

- The small fraction of applied glyphosate which reaches sites of phytotoxic action is related to the fact that the glyphosate must go through several barriers. Among these, one of the most important is believed to be the lipophilic cuticle on the
20 foliar surface to which the glyphosate is applied. It has therefore been theorized that it would be desirable to place the glyphosate into an amphiphilic medium which would provide greater compatibility between the lipophilic cuticle and the hydrophilic glyphosate, and thereby facilitate penetration of glyphosate into and through the cuticle. Similar thinking has been applied to other exogenous chemical substances,
25 particularly those typically formulated as water-soluble salts.

- That the concept of an amphiphilic medium as an aid to cuticular penetration and thereby enhanced biological effectiveness, for example of glyphosate, has validity is demonstrated by many studies in which foliar uptake or effectiveness has been enhanced by surfactants. An extensive study by Wyrill & Burnside, *Weed Science* 25,
30 275-287, 1977 led to a conclusion that "an effective surfactant is a critical component of any glyphosate spray mixture", but noted great variation among surfactant types in the degree of enhancement of herbicidal effectiveness afforded. The authors

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cautioned that "effectiveness of surfactant combinations was quite variable and difficult to predict" and that "the indiscriminate addition of surfactants or wetting agents to glyphosate spray mixtures which already contain a surfactant should be avoided". The Wyrill & Burnside study generally involved application of surfactants at very high rates relative to the rates of glyphosate applied. Under these conditions, and on the particular plant species they studied, the authors found that in general, cationic surfactants gave greater enhancement of the herbicidal effectiveness of glyphosate than did nonionic surfactants. It is well accepted by those of skill in the art that relative effectiveness of surfactants in enhancing biological activity of an exogenous chemical substance, particularly glyphosate, at high surfactant levels does not permit reliable prediction of relative effectiveness at much lower surfactant levels, as in the realm of the present invention.

Data are reported in International Publication No. WO 98/06259 for a wide variety of cationic, nonionic, anionic and amphoteric surfactants applied either in mixture with, or in sequence following, a glyphosate composition.

The term "alkyl", as used herein in relation to hydrophobic moieties of surfactants, has the broad meaning, as conventionally applied in surfactant art, of aliphatic hydrocarbyl, embracing unsaturated groups, for example alkenyl and alkynyl groups, as well as saturated alkyl groups, unless the context demands otherwise.

Surfactants having a hydrophilic moiety comprising one or more protonatable amino groups or cationic ammonium groups together with a total of 1 to about 100 oxyethylene units in one or more oxyethylene chains constitute a favored selection of surfactants useful in formulating glyphosate and other anionic exogenous chemical substances. For example, commercial glyphosate herbicide products marketed under the trademark Roundup® have been formulated with surfactant compositions based on polyoxyethylene C₈₋₂₂ alkylamines. For example, the surfactant composition MON 0818 of Monsanto Company, which has been extensively used in the formulation of Roundup® herbicide, contains a polyoxyethylene tallowamine having an average of about 15 oxyethylene units per molecule.

Numerous patents disclose compositions comprising glyphosate and an oxyethylene or polyoxyethylene amine or ammonium surfactant.

U.S. Patent No. 5,668,085 to Forbes *et al.* discloses compositions comprising

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- glyphosate and a polyoxyethylene C₈₋₂₂ alkylamine surfactant having an average of up to about 12 oxyethylene units per molecule. Australian Patent Application No. 57565/90 discloses compositions comprising glyphosate and a polyoxyethylene C₈₋₂₂ alkyldiaminopropane surfactant. U.S. Patent No. 5,317,003 to Kassebaum & Berk
- 5 discloses compositions comprising glyphosate and a quaternary polyoxyethylene C₆₋₁₄ alkylmethylammonium surfactant having about 5 to about 50 oxyethylene units per molecule. U.S. patent No. 5,652,197 to Claude *et al.* discloses compositions comprising glyphosate and a quaternary polyoxypropylene oxyethylene tri-(C₁₋₃ alkyl)ammonium surfactant having 2 to 20 oxypropylene units per molecule. U.S.
- 10 Patent No. 5,118,444 to Nguyen discloses compositions comprising glyphosate and a polyoxyethylene C₆₋₂₀ alkylamine oxide surfactant having about 5 to about 25 oxyethylene units per molecule. U.S. Patent No. 5,750,468 to Wright discloses compositions comprising glyphosate and a polyoxyethylene tertiary alkyletheramine, polyoxyethylene quaternary alkyletherammonium or polyoxyethylene alkyletheramine
- 15 oxide surfactant. French Patent Application No. 2 648 316 discloses compositions comprising glyphosate and a polyoxyethylene N-alkyl-1,3-diaminopropane surfactant.

- Polyoxyethylene C₁₆₋₂₂ alkylether surfactants have been less frequently disclosed in compositions with glyphosate, and generally at surfactant to glyphosate weight ratios outside the realm of the present invention. For example, European
- 20 Patent No. 0 206 537 discloses solid compositions comprising glyphosate and Plurafac™ A-39 surfactant of BASF, which is a polyoxyethylene C₁₆₋₁₈ alkylether surfactant having an average of about 55 oxyethylene units per molecule. The lowest weight ratio of Plurafac™ A-39 to glyphosate acid equivalent disclosed therein can be calculated as about 1.16:1 (composition 12 of Table IV of the cited patent).
- 25 Wyrill & Burnside, *op. cit.*, disclose plant treatment compositions comprising glyphosate and a 1:1 mixture of a polyoxyethylene alkylether surfactant identified as Plurafac™ A-46 with polyoxyethylene alkylamine surfactants Ethomeen™ T/15 of Akzo and MON 0818 of Monsanto, at surfactant to glyphosate ratios far outside the realm of the present invention. Probably because the surfactant concentration in the
- 30 compositions was so high (1% weight/volume), no significant benefit was evident for the mixtures over the alkylamine surfactants alone.

At lower surfactant to glyphosate weight ratios, strong enhancement of

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glyphosate herbicidal effectiveness has been reported for mixtures of a polyoxyethylene alkylamine or alkylammonium surfactant and a polyoxyethylene alkylether surfactant, where the alkylether is derived from a secondary alcohol, as in International Publication No. WO 95/16351, a Guerbet alcohol, as in U.S. Patent No. 5,663,117 to Warner, or an acetylenic diol, as in U.S. Patent No. 5,639,711 to Kassebaum *et al.* European Patent Application No. 0 582 561 discloses a solid granular glyphosate composition containing a polyoxyethylene quaternary alkylammonium surfactant (Ethoquad™ 18/25 of Akzo) and a polyoxyethylene C₁₃ alkylether surfactant (Trycol™ 5943 of Henkel) but does not report herbicidal effectiveness of this composition.

Townson, in her Ph.D. thesis, *Influence of formulation and application variables in relation to the performance of glyphosate and imazapyr for control of Imperata cylindrica (L.) Raeuschel*, University of Bristol, U.K., 312 pp., 1990, compared polyoxyethylene C₁₆₋₁₈ alkylethers having respectively 3, 12 and 19 oxyethylene units for enhancement of foliar retention, uptake, translocation and herbicidal effectiveness of glyphosate and imazapyr. Comparison was also made with polyoxyethylene alkylethers having shorter alkyl chain lengths (C₉₋₁₁, C₁₂₋₁₅ and C₁₃₋₁₅). The study further included polyoxyethylene alkylamine surfactants but no blends of alkylether and amine surfactants were tested.

It is an objective of the present invention to provide a new method of enhancing the biological effectiveness of an exogenous chemical substance, in particular an anionic exogenous chemical substance, applied to foliage of a plant.

Another object of the invention is to provide a useful alternative to existing methods for enhancing biological effectiveness of anionic exogenous chemical substances.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphical plot of the natural logarithm of amplitude of glyphosate proton NMR resonance, "ln(amplitude)", against the square of field gradient, "gradient²", for composition 24-04 of the present invention, as explained in Example 24. The plotted data form a curve that can be resolved into two straight-line components, one representing a free pool of glyphosate and one representing an

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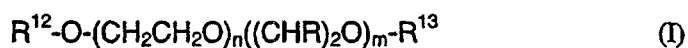
entrapped pool of glyphosate.

Figure 2 is a graphical plot of the fraction of glyphosate in the entrapped pool against the weight ratio of lecithin to MON 0818, as explained in Example 24.

SUMMARY OF THE INVENTION

5 In one embodiment of the present invention, a method is provided for eliciting biological activity of an anionic exogenous chemical substance applied to foliage of a plant, comprising

- (i) preparing a plant treatment composition that comprises
 - (a) water; having dissolved or dispersed therein
 - 10 (b) an anionic exogenous chemical substance in a biologically effective amount;
 - (c) an alkylether surfactant component consisting of one or more surfactants each having the formula (I)



15 wherein R^{12} is an aliphatic saturated or unsaturated hydrocarbyl group having about 16 to about 22 carbon atoms, n is an average number of about 5 to about 100, m is an average number of 0 to about 5, one R in each $-((CHR)_2O)-$ group is hydrogen and the other R is methyl, and R^{13} is a hydrogen, C_{1-4} alkyl or C_{2-4} acyl group; and

- (d) an amine surfactant component consisting of one or more surfactants each having a molecular structure that comprises

- (1) a hydrophobic moiety having one or a plurality of independently saturated or unsaturated, branched or
25 unbranched, aliphatic, alicyclic or aromatic C_{3-20} hydrocarbyl or hydrocarbylene groups joined together by 0 to about 7 ether linkages and having in total about 8 to about 24 carbon atoms, and
- (2) a hydrophilic moiety comprising an amino group that is
30 cationic or that can be protonated to become cationic, having attached directly thereto 1 to 3 oxyethylene groups or

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polyoxyethylene chains, these oxyethylene groups and
polyoxyethylene chains comprising on average 1 to about 50
oxyethylene units per surfactant molecule, the hydrophobic
moiety being attached either to the amino group or via an
5 ether linkage to an oxyethylene unit;

the weight ratio of the alkylether surfactant component to the amine
surfactant component being about 1:10 to about 10:1; wherein the
alkylether and amine surfactant components are present in total in an
adjuvant amount of about 0.05 to about 0.5 parts by weight per part by
10 weight of the anionic exogenous chemical substance, expressed as acid
equivalent; and

- (ii) applying a biologically effective amount of the plant treatment
composition to foliage of the plant;

whereby the alkylether and amine surfactant components interact synergistically to
15 elicit greater biological effectiveness of the anionic exogenous chemical substance
than would be elicited by either component alone at the same total surfactant
concentration in the plant treatment composition.

In another embodiment of the present invention, a method is provided for
eliciting biological activity of an anionic exogenous chemical substance applied to
20 foliage of a plant, comprising

- (i) preparing a plant treatment composition as described immediately above;
and
- (ii) applying a biologically effective amount of the plant treatment
composition to foliage of the plant within about 6 hours prior to rain or
25 activation of overhead irrigation on the plant.

In this embodiment, rainfastness of the composition has in many instances been found
to be surprisingly good.

In yet another embodiment of the present invention, a method is provided for
eliciting herbicidal activity of an anionic herbicide applied to foliage of a plant,
30 comprising

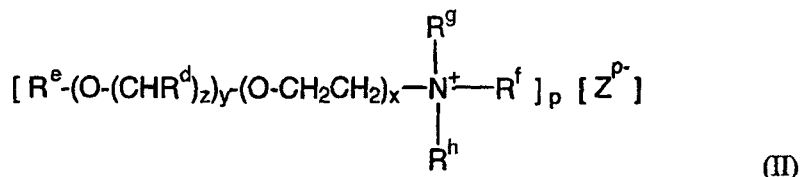
- (i) preparing a plant treatment composition that comprises
 - (a) water; having dissolved or dispersed therein

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- (b) a first herbicide that is anionic and is present in a herbicidally effective amount;
- (c) a second herbicide that is present in an amount effective to elicit a visible symptom of phytotoxicity in the plant within about 4 days after application to the foliage;
- (d) an alkylether surfactant component as described immediately above; and
- (e) an amine surfactant component as described immediately above; the weight ratio of the alkylether surfactant component to the amine surfactant component being about 1:10 to about 10:1; wherein the alkylether and amine surfactant components are present in total in an adjuvant amount of about 0.05 to about 0.5 parts by weight per part by weight of the first herbicide, expressed as acid equivalent; and
- (ii) applying a biologically effective amount of the plant treatment composition to foliage of the plant.

In this embodiment, a surprisingly low level of antagonism, or even total absence of antagonism, of the herbicidal effectiveness of the first herbicide by the presence of the second herbicide has been observed. The plant treatment composition used in this embodiment is itself an embodiment of the present invention.

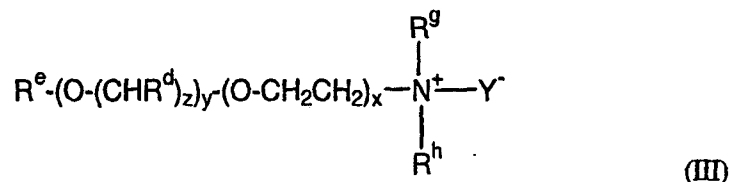
- 20 Amine surfactants useful in the present invention preferably have a chemical structure that, when present in an aqueous medium having a pH of about 4, can be individually represented by the formula (II)



- where R^e is hydrogen or a linear or branched C_{8-20} aliphatic hydrocarbyl group; each z is independently 2 or 3; each R^d is hydrogen or methyl whereby if z is 2 at least one R^d in the two $-(CHR^d)-$ groups is methyl; y is 0 to 7 such that the total number of carbon atoms in the group $R^e - (O - (CHR^d)_z)_y -$ is 8 to 24; x is 0 to 5; R^f is hydrogen, C_{1-4} alkyl or benzyl; R^g is C_{1-4} alkyl or $-(CH_2CH_2-O)_x R^c$ and R^h is C_{1-4} alkyl or $-(CH_2CH_2-O)_x R^c$, where R^c is hydrogen, C_{1-4} alkyl or C_{2-4} acyl and x' and x'' are

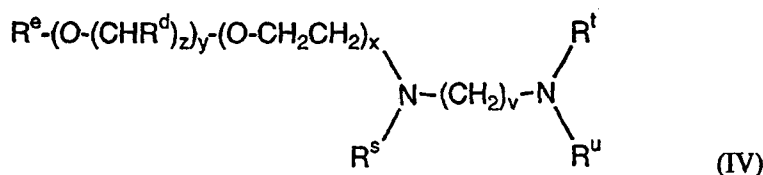
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average numbers such that $x + x' + x''$ (the total number of oxyethylene units in a molecule of the amine surfactant) is 1 to about 50; Z^{p-} is a suitable anion; and p is 1 or 2; or by the formula (III)



- 5 where R^d, R^e, R^g, R^h, x, y and z are as defined immediately above and Y^- is an anionic group selected from $-O^-$, $-(CHR^b)_w-COO^-$ and $-(CHR^b)_w-SO_3^-$ where w is 1 to 3 and each R^b is independently hydrogen, hydroxyl, C_{1-4} alkyl or hydroxy- $(C_{1-4}$ alkyl).

Other useful amine surfactants include those that can be represented by the formula (IV)



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where R^d, R^e, x, y and z are as defined immediately above, v is a number from 2 to 6, and R^s, R^t and R^u are independently C_{1-4} alkyl or $-(CH_2CH_2-O)_kR^c$ where R^c is hydrogen, C_{1-4} alkyl or C_{2-4} acyl and each k is an average number such that the total number of oxyethylene units in a molecule of the amine surfactant is 1 to about 50.

- 15 The alkylether surfactant(s) and the amine surfactant(s), when provided together as a surfactant mixture in a ratio in the indicated range, have been found generally to have at least one of the following unexpected effects:

- (i) the surfactants interact in a synergistic manner in enhancing biological effectiveness of the anionic exogenous chemical substance when the plant treatment composition is applied to foliage of a plant;
- 20 (ii) the surfactants together provide surprisingly enhanced rainfastness when the plant treatment composition is applied to foliage of a plant and rain falls or overhead irrigation is activated shortly (*e.g.*, within about 6 hours) after application;
- 25 (iii) the surfactants together unexpectedly reduce antagonism of biological effectiveness of the anionic exogenous chemical substance by a second

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exogenous chemical substance also present in the composition, in particular where the exogenous chemical substances are herbicides.

A "synergistic" interaction between one or more alkylether surfactants and one or more amine surfactants is to be understood herein as one satisfying the following test, notwithstanding any other definition of synergism that has been applied in the art. This test is conducted using a total amount of alkylether and/or amine surfactants that is a "suboptimal adjuvant amount" as defined herein. If such total amount of a mixture of alkylether and amine surfactants elicits biological effectiveness of a co-applied anionic exogenous chemical substance that is greater than the biological effectiveness elicited either by the same total amount of the alkylether surfactant(s) in the substantial absence of amine surfactant, or by the same total amount of the amine surfactant(s) in the substantial absence of alkylether surfactant, the alkylether and amine surfactant components of the mixture are considered to interact in a synergistic manner.

An "adjuvant amount" of a surfactant or mixture of surfactants is an amount sufficient, when applied to plant foliage together with an anionic exogenous chemical substance, to elicit a degree of biological effectiveness that is observably greater than that provided by the anionic exogenous chemical substance applied in the absence of any surfactant. A "suboptimal adjuvant amount" of a surfactant or mixture of surfactants is an adjuvant amount eliciting a degree of biological effectiveness that is observably less than that elicited by the same surfactant or mixture of surfactants in twice the amount. Surfactant amounts are conveniently expressed as weight/volume concentrations in aqueous plant treatment compositions and as weight/weight concentrations in liquid or solid concentrate compositions.

The present invention is not to be construed as being limited to situations where the surfactant mixture is used in a suboptimal adjuvant amount. Only the test for synergism between the alkylether and amine components of the surfactant mixture requires application in a suboptimal adjuvant amount.

It is further to be understood that the synergistic interaction between the alkylether and amine surfactants characteristic of compositions of the invention is not necessarily exhibited on all plant species or under all application conditions, being subject to the normal variability of complex biological phenomena. However, the

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generally superior biological effectiveness resulting from this synergistic interaction is exhibited with sufficient frequency and consistency to represent a major advance in the art.

By "rainfastness" herein is meant the degree to which biological effectiveness of an exogenous chemical substance is maintained when rain falls or overhead irrigation is activated shortly after foliar application of a plant treatment composition containing the exogenous chemical substance. Rainfastness can be measured by comparing biological effectiveness with and without rain or overhead irrigation. A suitable test for rainfastness involves overhead watering of treated plants by means of a sprinkler or spray system, in an amount of about 2.5 to about 25 mm at a rate of about 10 to about 100 mm/hour, beginning about 5 minutes to about 6 hours after application of the plant treatment composition; and recording biological effectiveness by comparison with treated plants not subjected to such overhead watering.

By "antagonism" herein is meant a reduction in biological effectiveness of a first exogenous chemical substance when applied in a plant treatment composition, such reduction resulting from the inclusion in the same plant treatment composition of a second exogenous chemical substance.

A plant treatment composition useful in the method of the invention can be provided to the end-user by a commercial manufacturer or formulator as a "ready-to-use" product. As an alternative, the plant treatment composition can be prepared by the end-user by dissolving, dispersing or diluting in water a first concentrate composition containing the anionic exogenous chemical substance, a second concentrate composition containing the alkylether component of the surfactant mixture and a third concentrate composition containing the amine component of the surfactant mixture. As a further alternative, the plant treatment composition can be prepared by the end-user by dissolving, dispersing or diluting in water a first concentrate composition containing the anionic exogenous chemical substance and a second concentrate composition containing the surfactant mixture. As a still further alternative, the plant treatment composition can be prepared by the end-user by dissolving, dispersing or diluting in water a single concentrate composition containing the anionic exogenous chemical substance and the surfactant mixture. Other ways of preparing the plant treatment composition will be apparent to those of skill in the art.

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Also useful in practice of the present invention is a concentrate composition for application in an aqueous carrier to foliage to elicit a biological effect, comprising about 10% to about 90% by weight of an anionic exogenous chemical substance expressed as acid equivalent (a.e.), together with an alkylether surfactant and an amine surfactant such that, when the concentrate composition is dissolved, dispersed or diluted in a suitable volume of water, a plant treatment composition useful in the method of the invention as provided above is formed. Such concentrate composition can be solid or liquid. A contemplated solid concentrate composition contains up to about 90% a.e. by weight of the exogenous chemical substance. A contemplated liquid concentrate composition contains up to about 50% by weight of the exogenous chemical substance expressed as acid equivalent (a.e.).

DETAILED DESCRIPTION OF THE INVENTION

The anionic exogenous chemical substance

Examples of anionic exogenous chemical substances that can be used in compositions useful in the method of the present invention include, but are not limited to, chemical pesticides (such as herbicides, algicides, fungicides, bactericides, viricides, insecticides, aphicides, miticides, nematocides and molluscicides), plant growth regulators, fertilizers and nutrients, gametocides, defoliants, desiccants, mixtures thereof and the like. Although the disclosure herein relates to "an anionic exogenous chemical substance", it is to be understood that more than one anionic exogenous chemical substance can be included if desired.

A preferred group of anionic exogenous chemical substances consists of those that are normally applied post-emergence to foliage of plants, i.e., foliar-applied anionic exogenous chemical substances. An especially preferred group of foliar-applied anionic exogenous chemical substances consists of those that are systemic in plants, that is, translocated to some extent from their point of entry in the foliage to other parts of the plant where they can usefully exert their desired biological effect.

Especially preferred among these are herbicides, plant growth regulators and nematocides, particularly those that have a molecular weight, excluding counterions, of less than about 300.

Among such compounds, an even more preferred category consists of

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nematicides such as those disclosed in U.S. Patent No. 5,389,680, the disclosure of which is incorporated herein by reference. Preferred nematicides of this group are 3,4,4-trifluoro-3-butenic acid or N-(3,4,4-trifluoro-1-oxo-3-butenyl)glycine.

In one embodiment, the anionic exogenous chemical substance is a herbicide.

- 5 Suitable herbicides include, without restriction, acifluorfen, asulam, benazolin, bentazon, bilanafos, bromacil, bromoxynil, chloramben, clopyralid, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, endothall, fenac, fenoxaprop, flamprop, fluazifop, flumiclorac, fluoroglycofen, fomesafen, fosamine, glufosinate, glyphosate, haloxyfop, imazameth, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin,
- 10 imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naptalam, nonanoic acid, picloram, quinclorac, quizalofop, sulfamic acid, 2,3,6-TBA, TCA and triclopyr. Especially preferred herbicides are those whose molecular structure comprises at least one of each of amine, carboxylate, and either phosphonate or phosphinate functional groups. This category includes the herbicides
- 15 N-phosphonomethylglycine (glyphosate) and DL-homoalanin-4-yl(methyl) phosphinate (glufosinate). Another preferred group of herbicides are those of the imidazolinone class, including imazameth, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin and imazethapyr.

The invention is illustrated herein by particular reference to glyphosate.

- 20 Although glyphosate has three acid sites, and can therefore form tribasic salts, preferred aqueous compositions have a pH value not greater than about 8, at which pH value the fraction of glyphosate existing as a tribasic salt is negligibly small. Only the two acid sites that are significantly deprotonated at pH 8 are therefore considered herein. One of these is on the phosphonate moiety, and the other is on the carboxylate
- 25 moiety, of the glyphosate molecule. At a pH of around 4 to 5, monovalent glyphosate anions predominate.

In plant treatment compositions useful in the method of the invention, the amount of anionic exogenous chemical substance present, in all forms thereof, is sufficient when applied to foliage of a plant to elicit the desired biological activity.

- 30 Such compositions are sometimes referred to as "spray compositions", "sprayable compositions" or "ready-to-use compositions" and typically contain about 0.02% by weight to about 2% by weight of the anionic exogenous chemical substance,

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expressed as acid equivalent (a.e.). For some purposes such compositions can contain up to about 5% a.e. by weight or even 10% a.e. by weight.

In concentrate compositions useful in practicing the invention, the amount of anionic exogenous chemical substance present, in all forms thereof, is sufficient, upon
5 dilution, dissolution or dispersion in a suitable volume of water to form a plant treatment composition, and upon application of the plant treatment composition to foliage of a plant, to elicit the desired biological activity.

As a significant portion of the cost of a packaged concentrate composition is the volume-related cost of packaging, transport and storage, it is desirable to increase
10 to the maximum practicable extent the concentration, or loading, of exogenous chemical substance in the composition. Generally the factor that limits loading of a liquid composition is physical stability of the composition under a range of storage conditions. The upper limit of loading, particularly in a liquid concentrate composition, depends on the nature and concentration of other ingredients in the
15 composition and can be readily determined by routine experimentation using procedures known in the art.

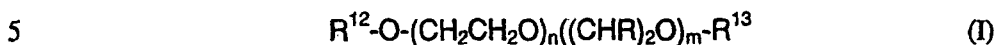
Although the anionic exogenous chemical substance can be present in its acid form, it is preferred that it be present predominantly in the form of a salt or mixture of salts. Preferably each such salt is water-soluble and has a cationic counterion of
20 molecular weight lower than about 100. In especially preferred water-soluble salts the cationic counterion is monovalent and is selected from alkali metal cations, ammonium cations, and organic ammonium and sulfonium cations having in total 1-6 carbon atoms.

In particular where the anionic exogenous chemical substance is glyphosate,
25 illustrative cationic counterions suitable for use in compositions of the invention are sodium, potassium, ammonium, dimethylammonium, isopropylammonium, monoethanolammonium and trimethylsulfonium cations.

Throughout this specification, all references to an anionic exogenous chemical substance in general can be taken to apply to glyphosate in particular, unless the
30 context demands otherwise.

22
177 180The alkylether surfactant

As indicated above, the alkylether surfactant component of compositions useful in the method of the invention comprises one or more surfactants each having the formula (I)



wherein R^{12} is an aliphatic saturated or unsaturated hydrocarbyl group having about 16 to about 22 carbon atoms, n is an average number of about 5 to about 100, m is an average number of 0 to about 5, one R in each $-(CHR)_2O-$ group is hydrogen and the other R is methyl, and R^{13} is a hydrogen, C_{1-4} alkyl or C_{2-4} acyl group.

10 Preferably R^{12} is linear, more preferably a linear C_{16} or C_{18} alkyl, alkenyl or alkadienyl group, for example a cetyl, stearyl, oleyl or linoleyl group. Advantageously the alkylether surfactant component is a mixture of surfactants having various R^{12} groups. For example, it may be a product described in cosmetic literature as "cetareth", wherein R^{12} groups are predominantly cetyl and stearyl groups.

15 Alternatively, the alkylether surfactant component can be derived from a natural oil or fat. For example, if the source is beef tallow, R^{12} groups are predominantly cetyl, stearyl and oleyl. If the source is corn oil or soybean oil, R^{12} groups are predominantly oleyl and linoleyl. If the source is palm oil, R^{12} groups are predominantly cetyl and oleyl. If the source is cottonseed oil, R^{12} groups are
20 predominantly cetyl, oleyl and linoleyl.

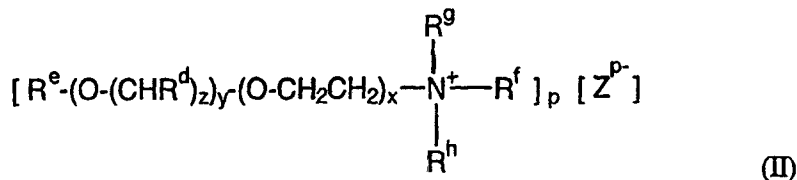
Preferably n (the average number of oxyethylene units) is about 7 to about 50, more preferably about 10 to about 40. Preferably m is 0 and R^{13} is hydrogen.

Among particularly preferred alkylether surfactants are ceteth-10, available for example as Brij™ 56 of ICI; ceteth-20, available for example as Brij™ 58 of ICI;
25 steareth-20, available for example as Brij™ 78 of ICI, Emthox™ 5888-A of Henkel and STA-20 of Heterene; steareth-30, available for example as STA-30 of Heterene; cetareth-20, available for example as Hetoxol™ CS-20 of Heterene; cetareth-27, available for example as Plurafac™ A-38 of BASF; and oleth-20, available for example as Brij™ 98 of ICI and Trycol™ 5971 of Henkel.

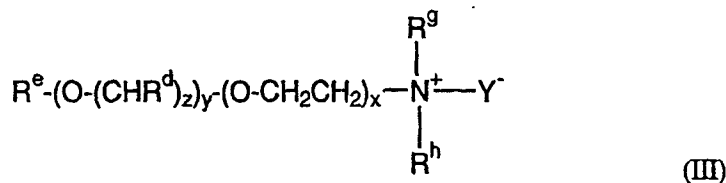
30 The amine surfactant

As indicated above, the amine surfactant component of compositions useful in the method of the invention preferably comprises one or more surfactants each having,

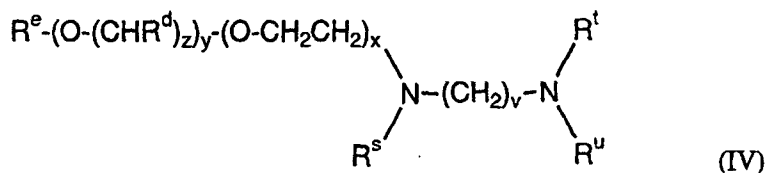
at a pH of about 4, the formula (II)



or the formula (III)



- 5 where R^e is hydrogen or a linear or branched C_{8-20} aliphatic hydrocarbyl group; each z is independently 2 or 3; each R^d is hydrogen or methyl whereby if z is 2 at least one R^d in the two $-(CHR^d)-$ groups is methyl; y is 0 to 7 such that the total number of carbon atoms in the group $R^e - (O - (CHR^d)_z)_y$ is 8 to 24; x is 0 to 5; R^f is hydrogen, C_{1-4} alkyl or benzyl; R^g is C_{1-4} alkyl or $-(CH_2CH_2-O)_x R^c$ and R^h is C_{1-4} alkyl or
- 10 $-(CH_2CH_2-O)_x R^c$, where R^c is hydrogen, C_{1-4} alkyl or C_{2-4} acyl and x' and x'' are average numbers such that $x + x' + x''$ (the total number of oxyethylene units in a molecule of the amine surfactant) is 1 to about 50; Z^{p-} is a suitable anion; p is 1 or 2; and Y^- is an anionic group selected from $-O^-$, $-(CHR^b)_w - COO^-$ and $-(CHR^b)_w - SO_3^-$ where w is 1 to 3 and each R^b is independently hydrogen, hydroxyl, C_{1-4} alkyl or
- 15 hydroxy- $(C_{1-4}$ alkyl). Other useful amine surfactants include those that can be represented by the formula (IV)



- where R^d , R^e , x , y and z are as defined immediately above, v is a number from 2 to 6, and R^s , R^t and R^u are independently C_{1-4} alkyl or $-(CH_2CH_2-O)_k R^c$ where R^c is
- 20 hydrogen, C_{1-4} alkyl or C_{2-4} acyl and each k is an average number such that the total number of oxyethylene units in a molecule of the amine surfactant is 1 to about 50.

When a maximum or minimum "average number" is recited herein with reference to a structural feature such as oxyethylene units, it will be understood by those skilled in the art that the integer number of such units in individual molecules in

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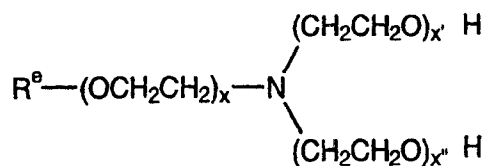
a surfactant preparation typically varies over a range that can include integer numbers greater than the maximum or smaller than the minimum "average number". The presence in a composition of individual surfactant molecules having an integer number of such units outside the stated range in "average number" does not remove the composition from the scope of the present invention, so long as the "average number" is within the stated range and other requirements are met.

Illustrative surfactant types that can be useful as part or all of the amine surfactant component of compositions useful in the method of the invention include the following:

10 (A) Surfactants of formulas (II) or (III) where R^c is a C_{8-20} aliphatic, saturated or unsaturated, linear or branched hydrocarbyl chain and y is 0. In this group R^c alone forms the hydrophobic moiety of the surfactant and is attached directly to the amine or ammonium group, as in alkylamines, or by an ether linkage formed by the oxygen atom of an oxyethylene group or the terminal oxygen atom of a polyoxyethylene chain, as in certain alkyletheramines. Illustrative subtypes having different hydrophilic moieties include:

15 (A-1) Surfactants of formula (II) wherein R^g is $-(CH_2CH_2-O)_x-H$ and R^h is $-(CH_2CH_2-O)_{x'}-H$ where $x' + x''$ is an average number of 2 to about 30, and R^f is hydrogen or methyl. This subtype includes commercial surfactants known in the art or referred to herein as "polyoxyethylene alkylamines" (where x is 0 and R^f is hydrogen), certain "polyoxyethylene alkyletheramines" (where x is 1-5 and R^f is hydrogen), and "polyoxyethylene N-methyl alkylammonium chlorides" (where x is 0, R^f is methyl, Z^p is a chloride anion and p is 1). Suitable examples are polyoxyethylene (2) cocoamine, polyoxyethylene (5) tallowamine, polyoxyethylene (10) cocoamine and polyoxyethylene (15) tallowamine, available for example from Akzo as Ethomeen™ C/12, Ethomeen™ T/15, Ethomeen™ C/20 and Ethomeen™ T/25 respectively, a surfactant conforming, when its amine group is non-protonated, to the formula

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where R^e is C₁₂₋₁₅ alkyl, x is 3 and x' + x'' is an average number of about 5, as disclosed in U.S. Patent No. 5,750,468, and polyoxyethylene (2) N-methyl cocoammonium chloride, polyoxyethylene (2) N-methyl stearylammmonium chloride, polyoxyethylene (10) N-methyl tallowammmonium chloride and polyoxyethylene (15) N-methyl cocoammonium chloride, available for example from Akzo as Ethoquad™ C/12, Ethoquad™ 18/12, Ethoquad™ T/20 and Ethoquad™ C/25 respectively. In cases where R^f is hydrogen, *i.e.*, in tertiary amine surfactants as opposed to quaternary ammonium surfactants, the anion Z^{p-} is typically not supplied with the surfactant. However, in a glyphosate-containing formulation at a pH of about 4-5, it will be recognized that the anion Z^{p-} can be an anion of the anionic exogenous chemical substance, for example glyphosate.

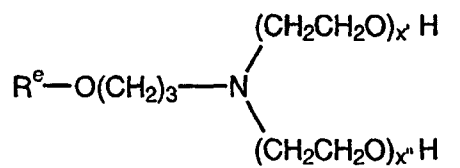
(A-2) Surfactants of formula (II) where x is 1-5, and R^f, R^g and R^h are independently C₁₋₄ alkyl. This subtype includes certain "polyoxyethylene N-methyl alkyletherammonium chlorides" (where R^f, R^g and R^h are each methyl, Z^{p-} is a chloride anion and p is 1).

(A-3) Surfactants of formula (III) wherein Y⁻ is an anionic oxide group. This subtype includes commercial surfactants known in the art or referred to herein as "polyoxyethylene alkylamine oxides" (where x is 0, R^g is -(CH₂CH₂-O)_xH and R^h is -(CH₂CH₂-O)_xH where x' + x'' is an average number of 2 to about 30), and certain "polyoxyethylene alkyletheramine oxides" (where x is 1-5, R^g is -(CH₂CH₂-O)_xH and R^h is -(CH₂CH₂-O)_xH where x' + x'' is an average number of 2 to about 30). Suitable examples are polyoxyethylene (2) cocoamine oxide, sold by Akzo as

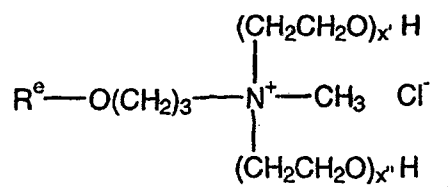
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Aromox™ C/12, and polyoxyethylene (10-20) tallowamine oxides, as disclosed in U.S. Patent No. 5,118,444.

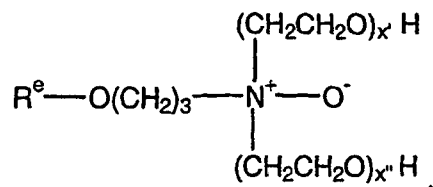
- (B) Surfactants of formulas (II) or (III) where R^e is a C₈₋₁₈ aliphatic, saturated or unsaturated, linear or branched hydrocarbyl chain, y is 1, z is 3, each R^d is hydrogen, and n is 0. In this group R^e-O(CH₂)₃- forms the hydrophobic moiety of the surfactant which is attached directly to the amine or ammonium group. These surfactants form a category of alkyletheramines as disclosed in U.S. Patent No. 5,750,468. Illustrative subtypes have the different hydrophilic moieties exemplified in (A-1) and (A-3) above. Suitable examples are a surfactant conforming, when its amine group is non-protonated, to the formula



a surfactant conforming to the formula



and a surfactant conforming to the formula

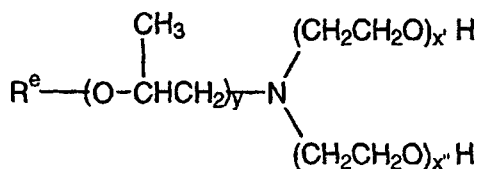


where, in each of the three formulas immediately above, R^e is C₁₂₋₁₅ alkyl and x' + x'' is an average number of about 5, as disclosed in U.S. Patent No. 5,750,468.

- (C) Surfactants of formula (II) or (III) where R^e is a C₈₋₁₈ aliphatic, saturated or unsaturated, linear or branched hydrocarbyl chain, y is 1-5, each -O-(CHR^d)_z- is a group -OCH(CH₃)CH₂- and x is 0. In this group R^e together with the -OCH(CH₃)CH₂- group or groups forms the

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hydrophobic moiety of the surfactant which is attached directly to the amino function. These surfactants form a further category of alkyletheramines as disclosed in U.S. Patent No. 5,750,468. Illustrative subtypes have the different hydrophilic moieties exemplified in (A-1) and (A-3) above. A suitable example is a surfactant of formula (II) conforming, when its amine group is non-protonated, to the formula



where R^e is C_{12-15} alkyl, y is 2 and $x' + x''$ is an average number of about 5, as disclosed in U.S. Patent No. 5,750,468.

- 10 (D) Surfactants of formula (II) where R^e is hydrogen, y is 3-8, each $-\text{O}-(\text{CHR}^d)_z-$ is a group $-\text{OCH}(\text{CH}_3)\text{CH}_2-$ and x is 1-3. In this group the polyether chain of $-\text{OCH}(\text{CH}_3)\text{CH}_2-$ groups (a polyoxypropylene chain) forms the hydrophobic moiety of the surfactant which is linked via one or more oxyethylene units to the amino function. In preferred surfactants
- 15 of this group, x is 1, and R^f , R^g and R^h are independently C_{1-4} alkyl. These surfactants are a subclass of the polyoxypropylene quaternary ammonium surfactants disclosed in U.S. Patent No. 5,652,197. In a suitable example, y is 7, x is 1, R^f , R^g and R^h are each methyl, Z^p is a chloride anion and p is 1.
- 20 (E) Surfactants of formula (IV) where R^e is a C_{8-18} aliphatic, saturated or unsaturated, linear or branched hydrocarbyl chain, x is 0, y is 0 and R^s , R^t and R^u are independently $-(\text{CH}_2\text{CH}_2-\text{O})_k\text{H}$ groups where each k is an average number such that Σk is 1 to about 50. This type includes surfactants known in the art or referred to herein as polyoxyethylene N-alkyl alkylenediamines. An illustrative example is polyoxyethylene
- 25 N-oleyl-1,3-diaminopropane having 3 oxyethylene units per molecule, as disclosed in French Patent Application No. 2 648 316.

In surfactants of formula (II), Z^p can be any suitable anion but preferably is chloride, bromide, iodide, sulfate, ethosulfate, phosphate, acetate, propionate,

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succinate, lactate, citrate or tartrate, or, as indicated above, an anion of the anionic exogenous chemical substance, for example glyphosate.

Presently the most preferred amine surfactants for use in compositions of the invention are polyoxyethylene (2-20) C₁₂₋₁₈ alkylamines and alkylammonium chlorides.

Amounts and ratios of alkylether and amine surfactants

The present invention is based in part on the unexpected discovery that biological effectiveness of an anionic exogenous chemical substance such as glyphosate herbicide in the presence of a mixture of alkylether and amine surfactants as defined herein can be significantly greater than that obtained in the presence of either the alkylether or the amine surfactant alone, at the same total surfactant concentration. The ratio of the alkylether surfactant component to the amine surfactant component producing this surprisingly synergistic interaction is not narrowly critical between about 1:10 and about 10:1 by weight. However, it will generally be found suitable to provide a ratio of about 1:5 to about 5:1, for example about 1:3 to about 3:1. An optimum ratio for particular surfactants, with a particular anionic exogenous chemical substance under particular conditions, can readily be determined by one of skill in the art by routine experimentation.

The present invention provides the greatest benefit where the amount of surfactant relative to the amount of anionic exogenous chemical substance applied is fairly low, specifically no higher than about 0.5 parts by weight of surfactant per part by weight of the anionic exogenous chemical substance, expressed as acid equivalent. At higher surfactant levels, typically either one of the surfactant components alone imparts a high degree of biological effectiveness and no great further advantage accrues from use of the mixture. At a surfactant rate lower than about 0.05 part by weight per part by weight of the anionic exogenous chemical substance, the synergistic interaction can be evident but the total amount of surfactant is normally insufficient to provide a useful magnitude of enhancement in biological effectiveness.

For example, where the anionic exogenous chemical substance is glyphosate, the greatest benefit of the invention is typically realized at a weight ratio of surfactant to glyphosate a.e. of about 0.1:1 to about 0.4:1.

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In a plant treatment composition useful in the method of the invention, the concentration of alkylether and amine surfactants together is preferably not greater than about 7.5 g/l, although higher concentrations can be used if desired. More preferably, the concentration of alkylether and amine surfactants together is about 0.5
5 to about 5 g/l, for example about 1 to about 3 g/l.

In a liquid concentrate composition useful in practicing the invention, the concentration of alkylether and amine surfactants together is typically about 25 to about 250 g/l, more typically about 50 to about 150 g/l. In a solid concentrate composition useful in practicing the invention, the concentration of alkylether and
10 amine surfactants together is typically about 3% to about 30% by weight, more typically about 6% to about 18% by weight.

Other ingredients

Compositions useful in the method of the invention can contain agriculturally acceptable materials other than an anionic exogenous chemical substance or salt
15 thereof, an alkylether surfactant and an amine surfactant.

For example, more than one anionic exogenous chemical substance can be included. For example, a glyphosate composition of the invention can optionally contain, in addition to glyphosate, any other anionic herbicide selected from those hereinbefore listed.

20 In a particular embodiment of the invention, glyphosate is present in a plant treatment composition together with a second anionic herbicide which is normally antagonistic to the biological effectiveness of glyphosate. The second anionic herbicide is typically one that produces visible symptoms of phytotoxicity in a treated plant within about 4 days after application to foliage. In preferred compositions useful
25 in this embodiment, the second anionic herbicide is glufosinate in the form of a salt or salts thereof. Glufosinate typically elicits symptoms of phytotoxicity in a treated plant more rapidly than glyphosate and often antagonizes the longer-term herbicidal effectiveness of glyphosate when the two herbicides are co-applied in a formulation or tank-mixture of prior art. Surprisingly and by contrast, such antagonism has generally
30 been found to be substantially reduced when glyphosate and glufosinate are accompanied by an alkylether and an amine surfactant in accordance with the present invention. It is contemplated that reduction in antagonism is a feature of compositions

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containing any two anionic exogenous chemical substances, one of which normally antagonizes the biological effectiveness of the other.

Illustratively in a composition useful in the method of the invention containing glyphosate and a second anionic herbicide, the a.e. weight ratio of the second anionic herbicidal substance, *e.g.*, glufosinate, to glyphosate can be about 1:1 to about 1:30, preferably about 1:2 to about 1:20.

A herbicidal composition useful in the method of the invention can optionally contain, in addition to an anionic herbicidal compound such as glyphosate or a salt thereof, a herbicidal compound that is other than anionic, such as for example an ester derivative of an anionic herbicide, or a herbicide selected from acetochlor, aclonifen, alachlor, ametryn, amidosulfuron, anilofos, atrazine, azafenidin, azimsulfuron, benfluralin, benfuresate, bensulfuron-methyl, bensulide, benzofenap, bifenox, bromobutide, bromofenoxim, butachlor, butamifos, butralin, butroxydim, butylate, cafenstrole, carbetamide, carfentrazone-ethyl, chlomethoxyfen, chlorbromuron, chloridazon, chlorimuron-ethyl, chlorotoluron, chlornitrofen, chlorotoluron, chlorpropham, chloresulfuron, chlorthal-dimethyl, chlorthiamid, cinmethylin, cinosulfuron, clethodim, clodinafop-propargyl, clomazone, clomeprop, cloransulam-methyl, cyanazine, cycloate, cyclosulfamuron, cycloxydim, cyhalofop-butyl, daimuron, desmedipham, desmetryn, dichlobenil, diclofop-methyl, diflufenican, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dinitramine, dinoterb, diphenamid, dithiopyr, diuron, EPTC, esprocarb, ethalfluralin, ethametsulfuron-methyl, ethofumesate, ethoxysulfuron, etobenzanid, fenoxaprop-ethyl, fenuron, flamprop-methyl, flazasulfuron, fluazifop-butyl, fluchloralin, flumetsulam, flumiclorac-pentyl, flumioxazin, fluometuron, fluorchloridone, fluoroglycofen-ethyl, flupoxam, flurenol, fluridone, fluroxypyr-1-methylheptyl, flurtamone, fluthiacet-methyl, fomesafen, halosulfuron, haloxyfop-methyl, hexazinone, imazosulfuron, indanofan, isoproturon, isouron, isoxaben, isoxaflutole, isoxapyrifop, lactofen, lenacil, linuron, mefenacet, metamitron, metazachlor, methabenzthiazuron, methylglyphosate, metobenzuron, metobromuron, metolachlor, metosulam, metoxuron, metribuzin, metsulfuron, molinate, monolinuron, naproanilide, napropamide, naptalam, neburon, nicosulfuron, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxyfluorfen, pebulate, pendimethalin,

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where the exogenous chemical substance is a herbicide, liquid nitrogen fertilizer or ammonium sulfate can be included in the composition. Ammonium sulfate and certain other inorganic ammonium salts are known to enhance herbicidal effectiveness of glyphosate and other herbicides on certain plant species.

5 Other optional components of compositions useful in the method of the invention include agents to modify color, odor, viscosity, gelling properties, freezing point, stability or texture.

One or more surfactant(s), other those of the classes specifically described above, can also be included in a contemplated composition. A wide range of
10 surfactants is available to the formulator of exogenous chemical substances and can be selected readily from standard works such as *McCutcheon's Emulsifiers and Detergents*, 1998 Edition, MC Publishing Company, or *Handbook of Industrial Surfactants*, 2nd Edition, Gower (1997).

There is no restriction on the type or chemical class of such additional
15 surfactant that can be used. Nonionic, anionic, cationic and amphoteric types, or combinations of more than one of these types, are all useful in particular situations. For example, soybean lecithin, which contains amphoteric acyl phosphatidylcholine surfactants, has been found useful in stabilizing certain liquid concentrate compositions as more particularly described below.

20 Another class of excipient material that can be useful in compositions useful in the method of the present invention is an oil, such as a triglyceride ester of fatty acids of animal, vegetable or synthetic origin, a paraffin, a polysiloxane, or a fatty acid or an ester or amide thereof. Natural triglyceride oils can be fractionated or not. Fractionation permits elimination of certain fatty acid chain lengths so as to modify
25 melting point.

In a particular embodiment of the invention, one or more oil(s) are included, each having a chemical structure corresponding to formula (V):



wherein R^4 is a hydrocarbyl group having about 5 to about 21 carbon atoms, R^5 is a
30 hydrocarbyl group having 1 to about 14 carbon atoms, the total number of carbon atoms in R^4 and R^5 is about 11 to about 27, and Q is O or NH. R^4 and R^5 are preferably linear hydrocarbyl chains. R^4 preferably has about 11 to about 21 carbon

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atoms and is preferably derived from a natural saturated or unsaturated fatty acid. R⁵ is preferably an alkyl group with 1 to about 6 carbon atoms. Especially preferred oils of formula (V) are therefore C₁₋₆ alkylesters or C₁₋₆ alkylamides of fatty acids.

5 In certain preferred embodiments, an oil is included that is a C₁₋₄ alkylester of a C₁₂₋₁₈ fatty acid, more preferably a C₁₋₄ alkylester of a C₁₂₋₁₈ saturated fatty acid. Examples include methyl oleate, ethyl oleate, isopropyl myristate, isopropyl palmitate and butyl stearate. Butyl stearate is especially preferred.

10 When present, one or more oil(s) of formula (V) are preferably included in a ratio of total weight of such oil(s) to weight of the anionic exogenous chemical substance, expressed as acid equivalent, of about 1:100 to about 1:1, though greater or lesser amounts can be found useful in particular situations.

15 Suitable concentrations of an oil of formula (V), if present, are about 0.001% to about 0.1% by weight in a plant treatment composition, and about 0.05% to about 5% by weight in a liquid concentrate composition. Higher or lower concentrations can be useful in particular situations.

Oil(s), if present, can be emulsified in a composition by means of the alkylether and/or amine surfactants. If desired, additional surfactant(s) can be included as emulsifier(s) for such oil(s).

20 Glycols form another class of excipient that can optionally be present in compositions useful in the method of the invention. For example, diethylene glycol and/or propylene glycol can be present as antifreezes, pour point depressants or in some other role. Polyglycols, such as polyethylene glycol having a molecular weight in the range from about 200 to about 800, especially about 400 to about 600, can also be useful for similar functions and/or as aids to inhibit gelling of the amine surfactant.

25 In preparing highly concentrated aqueous compositions useful in practicing the invention, certain coupling agents may be found beneficial in enhancing stability. These include low molecular weight alcohols such as ethanol, isopropanol and butanol, also dimethyl sulfoxide (DMSO), urea and tetrabutylammonium hydroxide.

30 Yet another class of excipient that can optionally be present is a solid microparticulate or nanoparticulate substance such as silica, which can serve as a stabilizer and/or thickener in liquid concentrate compositions.

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Concentrate compositions

- Although a plant treatment composition as described above can be prepared on-site as a dilute aqueous solution or dispersion immediately before application to foliage of a plant, a preferred embodiment of the invention involves dissolution, dispersion or dilution of a storage-stable concentrate composition. When dissolved or dispersed in, or diluted with, a suitable amount of water, such a concentrate composition forms a plant treatment composition useful in the method of the invention as described above. Thus the ratios of ingredients other than water defined for a plant treatment composition herein apply equally to a concentrate composition.
- Typically in preparing a plant treatment composition, one part by weight of a concentrate composition is added to about 9 to about 99 parts by weight of water; however greater or lesser amounts of water can be useful in particular situations.

- Concentrate compositions useful in practicing the invention can be solid or liquid. Formulation types known in the art to be generally suitable for foliar-applied anionic exogenous chemical substances are useful for the present invention. These include, without restriction, concentrated aqueous solutions and dispersions, emulsions (including oil-in-water, water-in-oil and water-in-oil-in-water types), microemulsions, suspension concentrates, emulsifiable concentrates, suspoemulsions, wettable powders, water-soluble powders and granules, water-dispersible powders and granules, *etc.*

- A solid concentrate composition useful in practicing the invention, such as a water-soluble or water-dispersible granule formulation, contains in total at least about 10% by weight and up to about 90% by weight of an anionic exogenous chemical substance expressed as acid equivalent. Preferably the content of exogenous chemical substance in a solid concentrate composition is about 25% to about 75%, more preferably about 50% to about 75%, a.e. by weight. Solid compositions are sometimes referred to as "dry" formulations; this should not be taken to imply that such compositions are entirely free of water or other liquid, merely that they feel dry to the touch.

- In accordance with one embodiment of the invention, a solid concentrate composition consists essentially of an anionic exogenous chemical substance or salt thereof, an alkylether surfactant and an amine surfactant as herein defined. In

accordance with another embodiment of the invention, a solid concentrate composition comprises these same ingredients together with other excipients. In accordance with a particular embodiment of the invention, a solid concentrate composition comprises an anionic exogenous chemical substance or salt thereof, an alkylether surfactant and an amine surfactant as herein defined, and ammonium sulfate. Preferred solid concentrate compositions are water-soluble or water-dispersible granules.

A liquid concentrate composition useful in practicing the invention, such as an aqueous solution or dispersion, contains in total at least about 10% by weight and up to about 50% or more by weight of an anionic exogenous chemical substance expressed as acid equivalent. Preferably the content of anionic exogenous chemical substance in a liquid concentrate composition is about 15% to about 45%, more preferably about 20% to about 40%, a.e. by weight. Weight/volume concentrations will vary depending on specific gravity of the liquid composition; however, typically the anionic exogenous chemical substance is present at about 180 to about 540 g a.e./l, more typically about 240 to about 480 g a.e./l.

Preferred liquid concentrate compositions have a continuous aqueous phase wherein is dissolved the anionic exogenous chemical substance in the form of a water-soluble salt thereof, forming an aqueous solution. The alkylether surfactant typically does not dissolve readily in this aqueous solution and instead forms a dispersed phase. The amine surfactant can be associated with the dispersed phase or distributed in the aqueous phase (for example as micelles) or both. The alkylether surfactant dispersion in such preferred compositions is stabilized by an emulsifying system, in which the amine surfactant can play a role. In one embodiment, the emulsifying system comprises acyl phosphatidylcholine, for example in the form of soybean lecithin, and an oil of formula (V) above, such as butyl stearate. Optionally a coupling agent such as a low molecular weight alcohol, DMSO, urea or tetrabutylammonium hydroxide can be included to enhance stability. This can be found especially beneficial when it is desired to increase the concentration of the anionic exogenous chemical substance to a high level, for example, in the case of glyphosate, above about 24% a.e. by weight.

Illustratively, a concentrate composition useful in this embodiment of the

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invention, wherein the anionic exogenous chemical substance is glyphosate in the form of its isopropylammonium (IPA) salt, the alkylether surfactant is cetareth-27 (e.g., Plurafac™ A-38 of BASF) and the amine surfactant is polyoxyethylene (15) tallowamine (e.g., Ethomeen™ T/25 of Akzo), has the following ingredients (all

5 percentages are by weight):

	glyphosate salt	24-48% (18-36% a.e.)
	cetareth-27	2-10%
	polyoxyethylene (15) tallowamine	2-10%
	soybean lecithin	1-10%
10	butyl stearate	0.5-10%
	coupling agent	0-5%
	water	to 100%

In liquid concentrate compositions useful in this embodiment of the invention, a fraction of the anionic exogenous chemical substance, for example glyphosate, is typically strongly associated with, or entrapped by, the dispersed phase. When the composition is diluted with water for foliar application, the fraction associated with or entrapped by the dispersed phase greatly declines; however, upon evaporation of water from a spray deposit on a leaf surface it is believed that association with or entrapment by supramolecular surfactant structures occurs again.

20 The association of glyphosate with supramolecular surfactant structures in liquid concentrate compositions of this embodiment is believed to be correlated with physical stability of the composition. Less physically stable compositions, for example those in which phase separation occurs within 24 hours when stored without agitation at 20-25°C, and in particular those with a relatively high weight ratio of amine surfactant to lecithin, typically show a lesser degree of glyphosate association with or entrapment by supramolecular surfactant structures.

Without being bound by theory, it is theorized that the strong association between glyphosate and supramolecular surfactant structures in compositions of this embodiment of the invention plays a role in enhancing glyphosate uptake across leaf cuticles. The association or entrapment is readily detectable by NMR spectroscopy techniques. One such technique involves the following illustrative procedure.

A sample of the liquid concentrate composition, conveniently about 200 to

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about 500 μ l, is placed in an NMR tube. A diffusion probe is used having a gradient coil capable of generating a linear field gradient of about 250 gauss/cm across the sample in response to a current pulse of 20 amp. Proton NMR spectra are recorded as a function of increasing field gradient. Data are collected using bipolar pulses and

5 LEDS pulse sequence to measure diffusion by the pulse field gradient method of Wu *et al.*, *Journal of Magnetic Resonance*, A115, 260-264, 1995.

The glyphosate resonance measured in the present procedure is that associated with the methylene group adjacent to the phosphonate moiety of the glyphosate molecule, which is well known in the art. Integrated intensity (amplitude) of the

10 glyphosate resonance is measured in each spectrum and the natural logarithm of such amplitude is plotted against the square of the field gradient. Data falling on a straight line in such a plot are indicative of simple diffusion in a one-component system. Data falling on a curve that can be resolved into two straight-line components, as in Figure

1, are indicative of a two-component system having two pools of glyphosate that

15 diffuse at different speeds. The faster-diffusing glyphosate represents the "free" pool, *i.e.*, glyphosate present in the aqueous medium, and the slower-diffusing glyphosate represents the "entrapped" pool, *i.e.*, glyphosate strongly associated with or entrapped by supramolecular aggregates formed by surfactants. The relative size of the two

pools can be estimated by extrapolating the linear fit of each straight-line component

20 to zero field gradient (the y-axis in the graph of Figure 1). The amount of glyphosate in a pool is proportional to the antilogarithm of the corresponding y-intercept value.

Certain aqueous concentrate compositions useful in practicing the invention can be described as stable dispersions. By "stable" in this context it is meant that no phase separation occurs during storage of a composition without agitation at 20-25°C

25 for 24 hours. The more desirable aqueous concentrate compositions are dispersions in which no phase separation occurs during storage without agitation at constant or varying temperatures from about 10°C to about 40°C for 48 hours, even more desirably from about 0°C to about 50°C for 7 days, and most desirably about -10°C to about 60°C for 30 days. Stability at elevated temperatures for short time periods

30 provides a good indication of long-term stability under normal storage conditions; it is contemplated that certain concentrate compositions useful in practicing the invention will be stable for periods of 1 year or more under normal storage conditions.

38
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Liquid concentrate compositions can be prepared by mixing the ingredients together in a suitable vessel. The degree of agitation required depends on the precise ingredients as will be understood by those of skill in the art; it will likewise be
5 recognized that certain ingredients require special treatment.

An aqueous concentrate composition containing lecithin and butyl stearate, as described above, can be prepared in the following illustrative way.

Lecithin is added to water in a suitable vessel and is fan-mixed, for example with a Variac mixer, set at 30% of maximum voltage, for about 10 minutes. This
10 results in the lecithin becoming hydrated. It is preferred to hydrate lecithin at an elevated temperature, for example around 50°C. To the hydrated lecithin in water are then added, in any order, the anionic exogenous chemical substance in the form of a water-soluble salt thereof, the alkylether surfactant, the amine surfactant and the butyl stearate. The vessel containing the resulting mixture is first agitated moderately, *e.g.*,
15 by hand shaking in the case of a small-scale preparation, and is then subjected to more vigorous mixing until homogeneous. This can be accomplished, for example, by fan-mixing with a Variac mixer, set at 30% of maximum voltage, for about 10 minutes. Alternatively, it can be accomplished by mixing with a Turrax mixer at 20,000 rpm for about 8 minutes. Optionally, the composition can then be microfluidized, for
20 example using a Model M-110F microfluidizer of Microfluidics International Corp., for 5 cycles at 15,000 psi (69 MPa).

Liquid concentrate compositions useful in practicing the invention are not limited to those prepared by the above procedure or a variant thereof. Other processes suitable for making a liquid concentrate composition are described in the Examples or
25 can be developed by one of skill in the art by routine experimentation.

Process for making a solid concentrate composition

A process for preparing a solid concentrate composition useful in practicing the invention comprises a first step of mixing an anionic exogenous chemical substance, or a salt thereof, or a mixture of such anionic exogenous chemical
30 substance and salt thereof, in solid particulate form with an alkylether surfactant and an amine surfactant, and optionally with other desired ingredients, together with sufficient water to form a wet mix of consistency suitable for further process steps as

described immediately below. The alkylether surfactant can be used in powder form or it can be melted prior to addition to the wet mix.

Such a process further comprises a second step of granulating the wet mix to form moist coherent granules, and a third step of drying the granules. Any granulating method known in the art to be suitable for the preparation of water-soluble or water-dispersible granules of an exogenous chemical substance can be used; preferred methods are pan granulation and extrusion granulation. The extrusion process described in United Kingdom Patent Application No. 1 433 882 is one illustrative process that can be useful in preparing granular compositions useful in practicing the present invention. Any drying method known in the art to be suitable for the preparation of water-soluble or water-dispersible granules of an exogenous chemical substance can be used; a preferred method is fluid-bed drying.

Solid concentrate compositions useful in practicing the invention are not limited to those prepared by the above procedure or a variant thereof. Other processes suitable for making a solid concentrate composition can be developed by one of skill in the art by routine experimentation.

Application of a plant treatment composition to foliage

Exogenous chemical substances are applied to plants at a rate sufficient to give the desired effect. These application rates are usually expressed as amount of exogenous chemical substance per unit area treated, e.g. grams per hectare (g/ha). What constitutes a "desired effect" varies according to the standards and practice of those who investigate, develop, market and use a specific class of exogenous chemical substances. For example, in the case of a herbicide, the amount applied per unit area to give, consistently and reliably, at least 85% control of a plant species as measured by growth reduction or mortality is often used to define a commercially effective rate.

Herbicidal effectiveness is one of the biological effects that can be enhanced through this invention. "Herbicidal effectiveness," as used herein, refers to any observable measure of control of plant growth, which can include one or more of the actions of (1) killing, (2) inhibiting growth, reproduction or proliferation, and (3) removing, destroying, or otherwise diminishing the occurrence and activity of plants.

The selection of application rates that are biologically effective for a specific anionic exogenous chemical substance is within the skill of the ordinary agricultural

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5 scientist. Those of skill in the art will likewise recognize that individual plant conditions, weather and growing conditions, as well as the specific anionic exogenous chemical substance and composition thereof selected, will influence the degree of biological effectiveness achieved in practicing this invention. Useful application rates for anionic exogenous chemical substances employed can depend upon all of the above conditions. With respect to the use of the method of this invention for glyphosate herbicide, much information is known about appropriate application rates. Over two decades of glyphosate use and published studies relating to such use have provided abundant information from which a weed control practitioner can select
10 glyphosate application rates that are herbicidally effective on particular species at particular growth stages in particular environmental conditions.

Herbicidal compositions of glyphosate or derivatives thereof are used to control a very wide variety of plants worldwide. Glyphosate compositions in accordance with the invention can be applied to a plant in a herbicidally effective
15 amount, and can effectively control one or more plant species of one or more of the following genera without restriction: *Abutilon*, *Amaranthus*, *Artemisia*, *Asclepias*, *Avena*, *Axonopus*, *Borreria*, *Brachiaria*, *Brassica*, *Bromus*, *Chenopodium*, *Cirsium*, *Commelina*, *Convolvulus*, *Cynodon*, *Cyperus*, *Digitaria*, *Echinochloa*, *Eleusine*, *Elymus*, *Equisetum*, *Erodium*, *Helianthus*, *Imperata*, *Ipomoea*, *Kochia*, *Lolium*,
20 *Malva*, *Oryza*, *Ottlochloa*, *Panicum*, *Paspalum*, *Phalaris*, *Phragmites*, *Polygonum*, *Portulaca*, *Pteridium*, *Pueraria*, *Rubus*, *Salsola*, *Setaria*, *Sida*, *Sinapis*, *Sorghum*, *Triticum*, *Typha*, *Ulex*, *Xanthium* and *Zea*.

Particularly important annual broadleaf species for which glyphosate compositions are used are exemplified without limitation by the following: velvetleaf
25 (*Abutilon theophrasti*), pigweed (*Amaranthus* spp.), buttonweed (*Borreria* spp.), oilseed rape, canola, indian mustard, etc. (*Brassica* spp.), commelina (*Commelina* spp.), filaree (*Erodium* spp.), sunflower (*Helianthus* spp.), morningglory (*Ipomoea* spp.), kochia (*Kochia scoparia*), mallow (*Malva* spp.), wild buckwheat, smartweed, etc. (*Polygonum* spp.), purslane (*Portulaca* spp.), russian thistle (*Salsola* spp.), sida
30 (*Sida* spp.), wild mustard (*Sinapis arvensis*) and cocklebur (*Xanthium* spp.)

Particularly important annual narrowleaf species for which glyphosate compositions are used are exemplified without limitation by the following: wild oat

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- (*Avena fatua*), carpetgrass (*Axonopus* spp.), downy brome (*Bromus tectorum*), crabgrass (*Digitaria* spp.), barnyardgrass (*Echinochloa crus-galli*), goosegrass (*Eleusine indica*), annual ryegrass (*Lolium multiflorum*), rice (*Oryza sativa*), ottochloa (*Ottochloa nodosa*), bahiagrass (*Paspalum notatum*), canarygrass (*Phalaris* spp.),
- 5 foxtail (*Setaria* spp.), wheat (*Triticum aestivum*) and corn (*Zea mays*).

Particularly important perennial broadleaf species for which glyphosate compositions are used are exemplified without limitation by the following: mugwort (*Artemisia* spp.), milkweed (*Asclepias* spp.), canada thistle (*Cirsium arvense*), field bindweed (*Convolvulus arvensis*) and kudzu (*Pueraria* spp.).

- 10 Particularly important perennial narrowleaf species for which glyphosate compositions are used are exemplified without limitation by the following: brachiaria (*Brachiaria* spp.), bermudagrass (*Cynodon dactylon*), yellow nutsedge (*Cyperus* ~~esculentus~~), purple nutsedge (*C. rotundus*), quackgrass (*Elymus repens*), lalang (*Imperata cylindrica*), perennial ryegrass (*Lolium perenne*), guineagrass (*Panicum*
- 15 *maximum*), dallisgrass (*Paspalum dilatatum*), reed (*Phragmites* spp.), johnsongrass (*Sorghum halepense*) and cattail (*Typha* spp.).

- Other particularly important perennial species for which glyphosate compositions are used are exemplified without limitation by the following: horsetail (*Equisetum* spp.), bracken (*Pteridium aquilinum*), blackberry (*Rubus* spp.) and gorse
- 20 (*Ulex europaeus*).

- Thus, the method of the invention where glyphosate is the anionic exogenous chemical substance can be useful on any of the above species. In a particular embodiment, a plant treatment composition as provided herein comprising glyphosate in the form of one or more salt(s) thereof is applied to foliage of crop plants
- 25 genetically transformed to tolerate glyphosate, and simultaneously to foliage of weeds or undesired plants growing in close proximity to such crop plants. This process results in control of the weeds or undesired plants while leaving the crop plants substantially unharmed. Crop plants genetically transformed to tolerate glyphosate include those whose seeds are sold by Monsanto or under license from Monsanto
- 30 bearing the Roundup Ready® trademark. These include varieties of cotton, soybean, canola and corn.

Application of plant treatment compositions to foliage of plants is preferably

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accomplished by spraying, using any conventional means for spraying liquids, such as spray nozzles or spinning-disk atomizers. The method of the present invention can be used in precision farming techniques, in which apparatus is employed to vary the amount of exogenous chemical substance applied to different parts of a field,

- 5 depending on variables such as the particular plant species present, plant growth stage, soil moisture status, *etc.* In one embodiment of such techniques, a global positioning system operated with the spraying apparatus can be used to control application of the composition in desired amounts to different parts of a field.

- A plant treatment composition is preferably dilute enough to be readily
10 sprayed using standard agricultural spray equipment. Suitable application rates for the present invention vary depending upon a number of factors, including the type and concentration of active ingredient and the plant species involved. Useful rates for applying an aqueous composition to a field of foliage can range from about 25 to about 1,000 liters per hectare (l/ha), preferably about 50 to about 300 l/ha, by spray
15 application.

EXAMPLES

- The following Examples are provided for illustrative purposes only and are not intended to limit the scope of the present invention. The Examples will permit better understanding of the invention and perception of its advantages and certain variations
20 of execution.

The following procedure was used for testing compositions of the Examples to determine herbicidal effectiveness, except where otherwise indicated.

- Seeds of the plant species indicated were planted in 85 mm square pots in a soil mix which was previously steam sterilized and prefertilized with a 14-14-14 NPK
25 slow release fertilizer at a rate of 3.6 kg/m³. The pots were placed in a greenhouse with sub-irrigation. About one week after emergence, seedlings were thinned as needed, including removal of any unhealthy or abnormal plants, to create a uniform series of test pots.

- The plants were maintained for the duration of the test in the greenhouse
30 where they received a minimum of 14 hours of light per day. If natural light was insufficient to achieve the daily requirement, artificial light with an intensity of

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approximately 475 microeinsteins was used to make up the difference. Exposure temperatures were not precisely controlled but averaged about 27°C during the day and about 18°C during the night. Plants were sub-irrigated throughout the test to ensure adequate soil moisture levels.

- 5 Pots were assigned to different treatments in a fully randomized experimental design with 3 replications. A set of pots was left untreated as a reference against which effects of the treatments could later be evaluated.

- 10 Application of glyphosate compositions was made by spraying with a track sprayer fitted with a 9501E nozzle calibrated to deliver a spray volume of 93 l/ha at a pressure of 166 kPa. After treatment, pots were returned to the greenhouse until ready for evaluation.

- 15 Treatments were made using dilute aqueous compositions. These could be prepared as spray compositions directly from their ingredients, or by dilution with water of preformulated concentrate compositions. All comparisons were made at equal glyphosate acid equivalent rates. The required degree of dilution for a glyphosate concentrate composition to make a plant treatment composition is calculated from the equation

$$A = RS/VC$$

- 20 where A is the volume in milliliters (ml) of the glyphosate composition to be added to the plant treatment composition being prepared, R is the desired glyphosate rate in grams of acid equivalent per hectare (g a.e./ha), S is the total volume in milliliters (ml) of plant treatment composition being prepared, V is the application rate in liters per hectare (l/ha) of plant treatment composition, conventionally referred to as "spray volume", and C is the concentration of glyphosate in grams of acid equivalent per liter (g a.e./l) in the glyphosate composition.

- 25 For evaluation of herbicidal effectiveness, all plants in the test were examined by a single practiced technician, who recorded percent inhibition, a visual measurement of the effectiveness of each treatment by comparison with untreated plants. Inhibition of 0% indicates no effect, and inhibition of 100% indicates that all of the plants are completely killed. Inhibition of 85% or more is in most cases considered acceptable for normal herbicidal use; however in greenhouse tests such as those of the Examples it is normal to include rates which give less than 85%

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inhibition, as this makes it easier to discriminate among compositions having different levels of effectiveness.

Example 1

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 1a. CS-20 of Heterene is cetareth-20 (polyoxyethylene C₁₆₋₁₈ alkylether having an average of 20 oxyethylene units per molecule). Plurafac™ A-38 of BASF is cetareth-27 (polyoxyethylene C₁₆₋₁₈ alkylether having an average of 27 oxyethylene units per molecule). Ethomeen™ T/25 of Akzo is polyoxyethylene tallowamine having an average of 15 oxyethylene units per molecule. The lecithin used was a soybean lecithin product of Avanti containing 45% phospholipid. All compositions of this Example are oil-in-water emulsions and were prepared by the following process.

Lecithin was first hydrated and dispersed in water as a 15% by weight stock by sonication using a Fisher Sonic Dismembrator, Model 550, fitted with a 2.4 cm probe tip with the pulse period set at 15 seconds with 1 minute intervals between pulses to allow cooling. Power output was set at level 8. Sonication was continued for 3 minutes (12 pulse periods).

Next, the required amounts of butyl stearate, lecithin and alkylether and/or amine surfactants were mixed thoroughly together, along with additional water if necessary. The alkylether surfactant was heated to bring it into a flowable condition before mixing. Then the required amount of glyphosate IPA salt (in the form of MON 0139, a 62% by weight aqueous solution of glyphosate IPA salt) was added to the resulting mixture with further agitation. The required amount of water was added to bring the concentration of glyphosate and other ingredients to the desired level. The composition was finally subjected to high-shear mixing using a Silverson L4RT-A mixer fitted with a medium emulsor screen, operated for 3 minutes at 7,000 rpm.

Table 1a

Concentrate composition	Glyphosate g a.e./l	Weight %				
		Lecithin	Butyl stearate	Ethomeen T/25	CS-20	Plurafac A-38
1-01	220	0.75	0.75	1.5		
1-02	220	0.75	0.75	1.5		

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Concentrate composition	Glyphosate g a.e./l	Weight %				
		Lecithin	Butyl stearate	Ethomeen T/25	CS-20	Plurafac A-38
1-03	220	0.75	0.75	3.0		
1-04	220	0.75	7.50	1.5		
1-05	220	0.75	7.50	3.0		
1-06	220	3.75	3.75	3.0		
1-07	220	1.50	1.50	3.0		
1-08	220	1.50	1.50	1.5		
1-09	220	3.75	3.75	1.5	1.5	
1-10	220	1.50	1.50	1.5	1.5	
1-11	220	3.75	7.50	1.5	1.5	
1-12	220	3.75	1.50	1.5	1.5	
1-13	220	0.75	3.75	1.5		1.5
1-14	220	0.75	7.50	1.5		1.5
1-15	220	0.75	3.75	3.0		3.0
1-16	220	0.75	7.50	3.0		3.0
1-17	220		7.50	3.0		
1-18	220	0.75	7.50			3.0

Glyphosate concentration in each of the above compositions was approximately 20% a.e. by weight. Thus the weight ratio of alkylether + amine surfactant to glyphosate a.e. was approximately 0.3:1 where total alkylether + amine surfactant concentration was 6% by weight, and approximately 0.15:1 where total alkylether + amine surfactant concentration was 3% by weight.

Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet, a form of barnyardgrass (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 23 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 18 days after application.

Two commercial concentrate formulations of glyphosate were diluted and applied as standard comparative treatments. These were Accord® herbicide of Monsanto, which consists essentially of 480 g/l glyphosate IPA salt (approximately 360 g a.e./l) in aqueous solution, and Roundup® Ultra herbicide of Monsanto, which contains 480 g/l glyphosate IPA salt (approximately 360 g a.e./l) in aqueous solution together with surfactant.

Results, averaged for all replicates of each treatment, are shown in Table 1b.

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Table 1b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Accord®	100	12	62
	200	5	55
	300	23	63
	400	43	78
Roundup® Ultra	100	27	82
	200	62	98
	300	88	95
	400	96	99
1-01	100	13	79
	200	68	95
	300	82	99
	400	95	91
1-02	100	27	82
	200	60	97
	300	81	95
	400	87	99
1-03	100	37	77
	200	62	96
	300	78	98
	400	89	90
1-04	100	37	84
	200	57	95
	300	84	99
	400	89	100
1-05	100	33	77
	200	65	100
	300	78	97
	400	88	97
1-06	100	43	78
	200	62	95
	300	87	97
	400	95	96
1-07	100	48	78
	200	80	91
	300	90	99
	400	76	93
1-08	100	48	83
	200	67	89
	300	86	96
	400	93	97

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
1-09	100	62	84
	200	82	98
	300	85	99
	400	91	97
1-10	100	63	80
	200	75	96
	300	85	99
	400	99	99
1-11	100	42	75
	200	78	98
	300	92	99
	400	93	100
1-12	100	52	80
	200	73	93
	300	86	99
	400	97	97
1-13	100	55	83
	200	75	97
	300	97	99
	400	92	99
1-14	100	52	87
	200	73	95
	300	91	97
	400	87	98
1-15	100	57	83
	200	92	96
	300	98	100
	400	100	98
1-16	100	79	88
	200	87	97
	300	99	99
	400	97	94
1-17	100	58	83
	200	47	94
	300	88	98
	400	91	93
1-18	100	58	87
	200	75	91
	300	83	99
	400	91	98

Outstanding herbicidal effectiveness was provided by composition 1-18,

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containing 3% of the alkylether surfactant Plurafac™ A-38. Addition of 3% of the amine surfactant Ethomeen™ T/25 (composition 1-16) further enhanced effectiveness. Composition 1-14, wherein the content of alkylether and amine surfactants were reduced to 1.5% each, surprisingly performed substantially equally to composition 1-18 (3% alkylether, no amine) and better than composition 1-05 (no alkylether, 3% amine). In all these compositions, lecithin content was 0.75% and butyl stearate content was 7.5%.

Perhaps because of the relatively high content of butyl stearate in these compositions, herbicidal effectiveness elicited by the alkylether surfactant was so high that a truly synergistic interaction between the alkylether and the amine surfactants was not able to be observed; however the excellent performance of composition 1-14 provides a strong hint of such interaction.

Example 2

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 2a. All are oil-in-water emulsions and were prepared by the process described in Example 1, except that for compositions 2-01 to 2-08 and 2-11 to 2-17 the lecithin was hydrated and dispersed not by ultrasonication but by microfluidizing, using a Model M-110F microfluidizer of Microfluidics International Corp., for 3 cycles.

Table 2a

Conc. comp.	Glyphosate g a.e./l	Weight %					
		Lecithin	Butyl stearate	Ethomeen T/25	MON 0818	CS-20	Plurafac A-38
2-01	220	0.75	3.75	3.0			3.0
2-02	220	0.75	0.75	3.0			3.0
2-03	220	0.75	3.75	3.0		3.0	
2-04	220	0.75	0.75	3.0		3.0	
2-05	220	6.00	1.50	3.0		3.0	
2-06	220	6.00	1.50	3.0			3.0
2-07	220	4.00	1.00	3.0		3.0	
2-08	220	4.00	1.00	3.0			3.0
2-09	220	0.75	3.75	3.0			3.0
2-10	220	0.75	0.75	3.0			3.0
2-11	220	0.75	3.75	6.0			
2-12	220	0.75	3.75			6.0	
2-13	345	6.00	1.50	4.5	4.5		

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Conc. comp.	Glyphosate g a.e./l	Weight %					
		Lecithin	Butyl stearate	Ethomeen T/25	MON 0818	CS-20	Plurafac A-38
2-14	345	6.00	1.50	6.0			3.0
2-15	345	6.00	1.50	6.0	6.0		
2-16	345	0.50	7.50	12.0			
2-17	345	6.00	1.50	4.5	4.5		3.0

Glyphosate concentration in compositions 2-01 to 2-12 was approximately 20% a.e. by weight. Glyphosate concentration in compositions 2-13 to 2-17 was approximately 30% a.e. by weight.

- 5 Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 19 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 15 days after application.

- 10 Accord® and Roundup® Ultra were diluted and applied as comparative treatments, as in Example 1. Results, averaged for all replicates of each treatment, are shown in Table 2b.

Table 2b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Accord®	150	45	82
	250	55	71
	350	80	72
	450	88	77
Roundup® Ultra	150	55	83
	250	89	88
	350	97	93
	450	99	93
2-01	150	92	83
	250	96	96
	350	99	96
	450	100	86
2-02	150	85	93
	250	97	78
	350	97	90
	450	99	90

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
2-03	150	87	85
	250	98	92
	350	99	95
	450	100	95
2-04	150	87	89
	250	97	92
	350	99	94
	450	99	91
2-05	150	87	77
	250	98	89
	350	99	93
	450	99	84
2-06	150	12	18
	250	96	73
	350	99	85
	450	99	84
2-07	150	82	89
	250	88	96
	350	96	98
	450	97	97
2-08	150	88	94
	250	95	90
	350	99	98
	450	99	98
2-09	150	94	94
	250	95	100
	350	97	99
	450	99	98
2-10	150	94	94
	250	98	99
	350	99	97
	450	99	96
2-11	150	83	81
	250	94	88
	350	98	93
	450	99	99
2-12	150	68	79
	250	95	96
	350	98	100
	450	99	98

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
2-13	150	86	98
	250	95	98
	350	99	100
	450	100	98
2-14	150	85	98
	250	98	98
	350	99	98
	450	100	98
2-15	150	86	95
	250	97	97
	350	99	95
	450	100	96
2-16	150	93	94
	250	98	98
	350	99	98
	450	100	97
2-17	150	95	96
	250	98	100
	350	100	100
	450	100	98

Outstanding herbicidal effectiveness was provided by composition 2-11, containing 6% of the amine surfactant Ethomeen™ T/25. Composition 2-12, containing 6% of the alkylether surfactant CS-20, was slightly less effective at the lowest glyphosate rate on ABUTH. Composition 2-03, containing 3% of each of Ethomeen™ T/25 and CS-20, was at least as effective as composition 2-11. In all these compositions, lecithin content was 0.75% and butyl stearate content was 3.75%.

Herbicidal effectiveness elicited by the amine surfactant in this test was so high that a truly synergistic interaction between the alkylether and the amine surfactants was not able to be observed; however the excellent performance of composition 2-03 provides a strong hint of such interaction.

Example 3

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 3a. All were prepared by the following process.

Alkylether surfactant (CS-20 or Plurafac™ A-38) and amine surfactant

(Ethomeen™ T/25) were added to water in a formulating vessel and the resulting mixture was heated to 55°C for 2 hours in a shaker bath. The mixture was allowed to cool, then glyphosate IPA salt, in the form of MON 0139, was added with mild agitation to form a preliminary glyphosate/surfactant mixture. Lecithin (Avanti, 45% phospholipids) was then added to this preliminary mixture, with stirring to break up lumps. The mixture was left for about 1 hour to allow the lecithin to hydrate, then butyl stearate was added with further stirring. Stirring continued until no phase separation occurred. The mixture in the formulating vessel was then transferred to a microfluidizer (Microfluidics International Corp., Model M-110F) and microfluidized for 3-5 cycles at 10,000 psi (69 MPa). In each cycle, the vessel was rinsed with microfluidized mixture. In the last cycle, the finished composition was collected in a clean vessel.

Table 3a

Conc. comp.	Glyphosate g a.e./l	Weight %				
		Lecithin	Butyl stearate	Ethomeen T/25	CS-20	Plurafac A-38
3-01	220	1.5	1.5	3.0	3.0	
3-02	220	1.5	1.5	3.0		3.0
3-03	220	1.5	1.5	6.0	3.0	
3-04	220	1.5	1.5	6.0		3.0
3-05	220	3.0	1.5	3.0	3.0	
3-06	220	3.0	1.5	3.0		3.0
3-07	348	1.5	1.5	6.0	3.0	
3-08	348	3.0	1.5	3.0	3.0	

Glyphosate concentration in compositions 3-01 to 3-06 was approximately 20% a.e. by weight. Glyphosate concentration in compositions 3-07 and 3-08 was approximately 30% a.e. by weight.

Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 17 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 18 days after application.

Accord® and Roundup® Ultra were diluted and applied as comparative treatments, as in Example 1. Results, averaged for all replicates of each treatment, are

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shown in Table 3b.

Table 3b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Accord®	100	28	32
	200	41	37
	300	73	64
	400	22	30
Roundup® Ultra	100	38	32
	200	82	73
	300	89	91
	400	97	89
3-01	100	51	40
	200	89	75
	300	96	92
	400	95	98
3-02	100	76	57
	200	98	81
	300	97	86
	400	96	98
3-03	100	69	60
	200	98	63
	300	95	82
	400	99	90
3-04	100	61	60
	200	94	84
	300	97	89
	400	99	97
3-05	100	64	53
	200	95	82
	300	96	90
	400	95	98
3-06	100	61	58
	200	94	78
	300	88	87
	400	100	94
3-07	100	56	61
	200	88	77
	300	91	82
	400	97	89
3-08	100	42	52
	200	82	80
	300	86	90
	400	97	92

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Compositions 3-01 to 3-08 of the invention exhibited a very high degree of herbicidal effectiveness on ABUTH and ECHCF, even by the high standard set by Roundup® Ultra.

5 Example 4

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 4a. Brij™ 78 of ICI is polyoxyethylene stearylether having an average of 20 oxyethylene units per molecule. Brij™ 700 of ICI is polyoxyethylene stearylether having an average of 100 oxyethylene units per molecule. MON 0818 of Monsanto is a surfactant based on polyoxyethylene tallowamine having an average of 15 oxyethylene units per molecule.

Compositions 4-01 to 4-04 and 4-08 were prepared as follows. Glyphosate IPA salt in the form of MON 0139 was added in the desired amount to a weighed quantity of alkylether and/or amine surfactant. Heat was applied to the alkylether surfactant to bring it into a flowable condition before adding MON 0139. The required amount of water was then added to bring the concentration of glyphosate and other ingredients to the desired level. The composition was finally subjected to high-shear mixing using a Silverson L4RT-A mixer fitted with a medium emulsor screen, operated for 3 minutes at 7,000 rpm.

Compositions 4-05 to 4-07 and 4-09 to 4-18 contained a colloidal particulate silica and were prepared as follows. The required amount of the selected silica was suspended in a concentrated glyphosate IPA salt solution (MON 0139) and agitated with cooling to ensure homogeneity of the resulting glyphosate/silica mixture. In the case of compositions 4-09 to 4-18 that also contained alkylether and amine surfactants, the selected surfactants were added in the required amount by weight. Heat was applied to the alkylether surfactant to bring it into a flowable condition before adding to the glyphosate/silica mixture. The required amount of water was then added to bring the concentration of glyphosate and other ingredients to the desired level. The composition was finally subjected to high-shear mixing using a Silverson L4RT-A mixer fitted with a medium emulsor screen, operated for 3 minutes at 7,000 rpm.

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The following types of silica were used, all from Degussa: A = Aerosil™ 380; B = Aerosil™ MOX-80; C = Aerosil™ MOX-170.

All compositions of this Example except compositions 4-01 to 4-03 were acceptably storage-stable.

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Table 4a

Concentrate composition	Glyphosate g a.e./l	Weight %				Type of silica
		Brij 78	Brij 700	MON 0818	silica	
4-01	488	3.0				
4-02	488	4.5				
4-03	488	6.0				
4-04	488			3.0		
4-05	488				1.5	A
4-06	488				1.5	B+C (1:1)
4-07	488				3.0	A+B (1:1)
4-08	488		1.5			
4-09	488	3.0		3.0	1.5	A
4-10	488	4.5		3.0	1.5	A
4-11	488	6.0		3.0	1.5	A
4-12	488	3.0		3.0	1.5	B+C (1:1)
4-13	488	4.5		3.0	1.5	B+C (1:1)
4-14	488	6.0		3.0	1.5	B+C (1:1)
4-15	488	3.0		3.0	1.5	A+B (1:1)
4-16	488	4.5		3.0	1.5	A+B (1:1)
4-17	488	6.0		3.0	1.5	A+B (1:1)
4-18	488		4.5	3.0	1.5	B+C (1:1)

Glyphosate concentration in all compositions was approximately 40% a.e. by weight.

10 Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 16 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 21 days after application.

15 Accord® and Roundup® Ultra were diluted and applied as comparative treatments, as in Example 1. Results, averaged for all replicates of each treatment, are shown in Table 4b.

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Table 4b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Accord®	100	2	23
	200	18	50
	300	42	67
	400	63	80
Roundup® Ultra	100	20	47
	200	40	86
	300	83	98
	400	93	98
4-01	100	10	75
	200	62	83
	300	80	96
	400	93	99
4-02	100	40	60
	200	77	92
	300	87	97
	400	93	99
4-03	100	23	40
	200	38	63
	300	78	91
	400	97	91
4-04	100	20	38
	200	23	77
	300	43	94
	400	73	94
4-05	100	7	30
	200	25	37
	300	42	60
	400	67	63
4-06	100	7	30
	200	20	53
	300	52	67
	400	83	67
4-07	100	5	35
	200	20	63
	300	57	80
	400	43	85
4-08	100	22	83
	200	47	99
	300	86	98
	400	78	100

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
4-09	100	12	45
	200	25	77
	300	40	83
	400	37	95
4-10	100	13	53
	200	73	99
	300	85	98
	400	99	99
4-11	100	25	50
	200	60	88
	300	93	99
	400	99	99
4-12	100	25	45
	200	57	88
	300	85	97
	400	100	94
4-13	100	30	52
	200	68	87
	300	93	99
	400	100	92
4-14	100	40	45
	200	73	88
	300	81	98
	400	100	99
4-15	100	8	57
	200	33	96
	300	81	99
	400	95	99
4-16	100	10	62
	200	48	83
	300	99	98
	400	100	100
4-17	100	27	58
	200	65	92
	300	75	98
	400	93	99
4-18	100	5	40
	200	33	87
	300	55	98
	400	75	98

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216Example 5

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 5a.

- 5 Compositions 5-12 to 5-14 were prepared in the same way as compositions 4-01 to 4-04 and 4-08 of Example 4. Compositions 5-01 to 5-11 and 5-15 to 5-17 were prepared in the same way as compositions 4-09 to 4-18 of Example 4. The following types of silica were used, all from Degussa: A = Aerosil™ 380; B = Aerosil™ MOX-80; C = Aerosil™ MOX-170.

Table 5a

Conc. comp.	Glyphosate g a.e./l	Weight %				Type of silica
		Brij 78	Ethomeen T/25	propylene glycol	silica	
5-01	488	3.0			0.8	A
5-02	488	6.0			1.5	B+C (1:1)
5-03	488	4.5			1.5	A
5-04	488	4.5	2.25	0.5	1.5	A+B (2:1)
5-05	488	4.5		0.5	1.5	A+B (2:1)
5-06	488	6.0		0.5	1.5	A+B (2:1)
5-07	488	3.0	1.50	0.5	1.5	A+B (2:1)
5-08	488	6.0	3.00	0.5	1.5	A+B (2:1)
5-09	488	3.0	1.50	0.5	1.5	A
5-10	488	4.5	2.25	0.5	1.5	A
5-11	488	6.0	3.00	0.5	1.5	A
5-12	488		1.50	0.5		
5-13	488		2.25	0.5		
5-14	488		3.00	0.5		
5-15	488		1.50	0.5	1.5	A+B (2:1)
5-16	488		2.25	0.5	1.5	A+B (2:1)
5-17	488		3.00	0.5	1.5	A+B (2:1)

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Glyphosate concentration in all compositions was approximately 40% a.e. by weight.

- 15 Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 16 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 20 days after application.

Accord® and Roundup® Ultra were diluted and applied as comparative treatments, as in Example 1. Results, averaged for all replicates of each treatment, are shown in Table 5b.

Table 5b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Accord®	100	0	3
	200	10	12
	300	43	22
	400	47	27
Roundup® Ultra	100	13	15
	200	25	22
	300	58	53
	400	68	82
5-01	100	30	20
	200	60	53
	300	73	88
	400	87	96
5-02	100	40	23
	200	63	55
	300	88	87
	400	93	93
5-03	100	42	20
	200	72	55
	300	82	83
	400	90	88
5-04	100	60	32
	200	70	57
	300	90	88
	400	90	93
5-05	100	47	32
	200	67	57
	300	88	85
	400	94	88
5-06	100	33	37
	200	68	67
	300	82	80
	400	90	88
5-07	100	35	37
	200	67	70
	300	87	85
	400	97	93

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
5-08	100	32	35
	200	67	77
	300	85	92
	400	97	95
5-09	100	27	33
	200	57	67
	300	88	83
	400	93	95
5-10	100	13	33
	200	62	58
	300	80	80
	400	92	92
5-11	100	13	20
	200	60	57
	300	88	63
	400	93	82
5-12	100	10	27
	200	53	53
	300	70	67
	400	88	85
5-13	100	3	28
	200	50	57
	300	67	70
	400	90	82
5-14	100	3	28
	200	55	57
	300	70	83
	400	87	87
5-15	100	10	20
	200	58	43
	300	70	72
	400	83	85
5-16	100	12	22
	200	55	57
	300	73	77
	400	92	90
5-17	100	7	20
	200	53	55
	300	70	75
	400	85	88

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219Example 6

Plant treatment compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 6a.

- Compositions 6-01 to 6-08 are each representative of five plant treatment compositions prepared to provide glyphosate a.e. rates of 100, 200, 300, 400 and 500 g a.e./ha when applied at 93 l/ha. Weight ratio of total surfactant to glyphosate a.e. was kept constant across all five glyphosate a.e. rates. Ratios shown in Table 6a are on an "active" surfactant basis, not an "as is" surfactant basis, with respect to Arquad™ C-50, which is supplied at 50% concentration. The plant treatment compositions were prepared by simply mixing the ingredients in water at the required dilution. Glyphosate IPA salt was supplied as MON 0139. Plurafac™ A-38 of BASF is a polyoxyethylene C₁₆₋₁₈ alkylether surfactant having an average of about 27 oxyethylene units per molecule. Arquad™ C-50 of Akzo is a quaternary cocoalkyltrimethylammonium chloride surfactant having no oxyethylene units. MON 0818 of Monsanto is a surfactant based on polyoxyethylene tallowamine having an average of about 15 oxyethylene units per molecule.

Table 6a

Composition	Weight ratio of total surfactant/glyphosate a.e.	Surfactant(s) (weight ratio)
6-01	0.4:1	Plurafac A-38
6-02	0.4:1	Plurafac A-38 + Arquad C-50 (10:1)
6-03	0.4:1	Plurafac A-38 + Arquad C-50 (2:1)
6-04	0.4:1	Plurafac A-38 + Arquad C-50 (1:1)
6-05	0.4:1	Plurafac A-38 + Arquad C-50 (1:2)
6-06	0.4:1	Plurafac A-38 + Arquad C-50 (1:10)
6-07	0.4:1	Arquad C-50
6-08	0.4:1	Plurafac A-38 + MON 0818 (1:1)

- Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 15 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 19 days after application.

- MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Two sets of replicated pots were sprayed with Roundup® Ultra, as the

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first and last set of treatments applied. Results, averaged for all replicates of each treatment, are shown in Table 6b.

Table 6b

Plant treatment composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
MON 0139	100	2	50
	200	3	30
	300	6	55
	400	6	65
	500	27	65
Roundup® Ultra (first set)	100	12	0
	200	6	52
	300	47	65
	400	72	70
	500	83	73
Roundup® Ultra (second set)	100	4	38
	200	5	42
	300	30	63
	400	60	78
	500	68	81
6-01	100	1	33
	200	9	57
	300	48	70
	400	73	70
	500	73	82
6-02	100	4	48
	200	11	63
	300	31	68
	400	68	78
	500	75	97
6-03	100	0	23
	200	5	57
	300	9	68
	400	62	82
	500	67	79
6-04	100	5	10
	200	17	63
	300	16	68
	400	67	68
	500	72	77

Plant treatment composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
6-05	100	5	27
	200	7	53
	300	47	63
	400	63	73
	500	73	80
6-06	100	4	47
	200	6	53
	300	20	62
	400	50	68
	500	70	78
6-07	100	7	48
	200	4	52
	300	7	63
	400	15	88
	500	48	80
6-08	100	2	63
	200	12	72
	300	47	82
	400	68	86
	500	77	100

The synergistic interaction apparent from the data of Wyrill & Burnside, *op. cit.*, between Plurafac™ A-46 and Arquad™ C-50, at very high surfactant to glyphosate a.e. ratios, was not evident in this test using Plurafac™ A-38 and Arquad™ C-50 at surfactant to glyphosate a.e. ratios in the realm of the present invention, which are much lower than those of Wyrill & Burnside.

Example 7

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 7a.

Compositions 7-01 to 7-05 were prepared by mixing the ingredients in water and agitating the mixture in a shaker bath at 50°C for 30 minutes. Ethoquad™ C/25 of Akzo is a polyoxyethylene quaternary N-methyl cocoalkylammonium chloride surfactant having an average of about 15 oxyethylene units per molecule. Ethoquad™ 18/25 of Akzo is a polyoxyethylene quaternary N-methyl stearyl ammonium chloride surfactant having an average of about 15 oxyethylene units per molecule.

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Table 7a

Concentrate composition	Glyphosate g a.e./l	Weight %		
		Plurafac A-38	Ethoquad C/25	Ethoquad 18/25
7-01	62	3.0		
7-02	62	2.1	0.9	
7-03	62	1.5	1.5	
7-04	62	2.1		0.9
7-05	62	1.5		1.5

Glyphosate concentration in all compositions was approximately 6% a.e. by weight.

- 5 Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above, except that 6 replicate pots of each species were subjected to each treatment, applied in two sets of three pots. Evaluation of herbicidal effectiveness was done 14 days after application.

- 10 MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for all replicates of each treatment, are shown in Table 7b.

Table 7b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
MON 0139	100	6	40
	200	48	52
	300	65	62
	400	70	64
	500	85	68
Roundup® Ultra	100	63	56
	200	82	77
	300	91	84
	400	96	91
	500	97	96
7-01	100	76	61
	200	89	81
	300	96	94
	400	97	96
	500	99	97

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
7-02	100	77	72
	200	93	92
	300	97	96
	400	98	94
	500	99	96
7-03	100	78	68
	200	94	89
	300	96	95
	400	98	97
	500	98	97
7-04	100	80	71
	200	91	86
	300	97	90
	400	98	92
	500	98	94
7-05	100	79	71
	200	94	93
	300	96	94
	400	98	94
	500	98	96

Compositions 7-02 to 7-05, each containing both an alkylether surfactant (Plurafac™ A-38) and an amine surfactant (Ethoquad™ C/25 or 18/25) as required by the present invention, exhibited greater herbicidal effectiveness in this test than composition 7-01, containing only the alkylether component but at the same total surfactant concentration.

Example 8

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 8a.

Compositions 8-01 to 8-06 were prepared by mixing the ingredients in water and agitating the mixture in a shaker bath at 50°C for 30 minutes. Hetoxol™ CS-25 of Heterene is a polyoxyethylene C₁₆₋₁₈ alkylether surfactant having an average of about 25 oxyethylene units per molecule. Plurafac™ A-38 of BASF is a polyoxyethylene C₁₆₋₁₈ alkylether surfactant having an average of about 27 oxyethylene units per molecule. Ethomeen™ T/25 of Akzo is a polyoxyethylene quaternary tallowamine surfactant having an average of about 15 oxyethylene units

per molecule. Trymeen™ 6617 of Henkel is a polyoxyethylene quaternary tallowamine surfactant having an average of about 50 oxyethylene units per molecule.

Table 8a

Conc. comp.	Glyphosate g a.e./l	Weight %			
		Plurafac A-38	Hetoxol CS-25	Ethomeen T/25	Trymeen 6617
8-01	62	3.0			
8-02	62	1.5		1.5	
8-03	62		3.0		
8-04	62		1.5	1.5	
8-05	62		1.5		1.5
8-06	62				3.0

- 5 Glyphosate concentration in all compositions was approximately 6% a.e. by weight.

Velvetleaf (*Abutilon theophrasti*, ABUTH) plants were grown and treated by the standard procedures given above, except that 6 replicate pots were subjected to each treatment, applied in two sets of three pots. Applications of plant treatment compositions were made 15 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application.

MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for all replicates of each treatment, are shown in Table 8b.

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Table 8b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition
		ABUTH
MON 0139	100	0
	200	5
	300	52
	400	71
	500	77
Roundup® Ultra	100	2
	200	42
	300	78
	400	84
	500	92

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition
		ABUTH
8-01	100	3
	200	52
	300	79
	400	88
	500	93
8-02	100	13
	200	58
	300	75
	400	96
	500	97
8-03	100	7
	200	57
	300	77
	400	89
	500	94
8-04	100	5
	200	49
	300	82
	400	90
	500	95
8-05	100	14
	200	60
	300	76
	400	91
	500	94
8-06	100	1
	200	21
	300	71
	400	83
	500	92

Example 9

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 9a.

5 Compositions 9-01 to 9-04 were prepared by mixing the ingredients in water and agitating the mixture in a shaker bath at 50°C for 30 minutes. Concentrations of Arquad™ T-50, which is supplied at 50% concentration, are shown in Table 9a on an "active" surfactant basis, not an "as is" surfactant basis. Arquad™ T-50 of Akzo is a quaternary tallowalkyltrimethylammonium chloride surfactant having no oxyethylene

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units. Ethoquad™ C/25 of Akzo is a polyoxyethylene quaternary N-methyl cocoalkylammonium chloride surfactant having an average of about 15 oxyethylene units per molecule. Ethoquad™ 18/25 of Akzo is a polyoxyethylene quaternary N-methyl stearyl ammonium chloride surfactant having an average of about 15

5 oxyethylene units per molecule.

Table 9a

Conc. comp.	Glyphosate g a.e./l	Weight %			
		Plurafac A-38	Arquad T-50	Ethoquad C/25	Ethoquad 18/25
9-01	62	3.0			
9-02	62	1.5	1.5		
9-03	62	1.5		1.5	
9-06	62	1.5			1.5

Glyphosate concentration in all compositions was approximately 6% a.e. by weight.

10 Velvetleaf (*Abutilon theophrasti*, ABUTH) plants were grown and treated by the standard procedures given above, except that 6 replicate pots were subjected to each treatment, applied in two sets of three pots. Applications of plant treatment compositions were made 19 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application.

15 MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for all replicates of each treatment, are shown in Table 9b.

Table 9b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition
		ABUTH
MON 0139	100	6
	200	12
	300	58
	400	72
	500	80
Roundup® Ultra	100	8
	200	64
	300	77
	400	81
	500	89

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition
		ABUTH
9-01	100	57
	200	76
	300	81
	400	83
	500	93
9-02	100	11
	200	75
	300	77
	400	86
	500	92
9-03	100	55
	200	76
	300	84
	400	91
	500	97
9-04	100	58
	200	76
	300	84
	400	92
	500	94

5 A mixture of the alkylether surfactant Plurafac™ A-38 with an amine surfactant having no oxyethylene units (Arquad™ T-50, composition 9-02) elicited significantly lower herbicidal effectiveness with glyphosate than a similar mixture with a polyoxyethylene amine surfactant (Ethoquad™ C/25 or 18/25, compositions 9-03 and 9-04 respectively).

Example 10

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 10a.

10 Compositions 10-01 to 10-06 were prepared by mixing the ingredients in water and agitating the mixture in a shaker bath at 50°C for 30 minutes.

Table 10a

Concentrate composition	Glyphosate g a.e./l	Weight %	
		Hetoxol CS-25	Ethoquad 18/25
10-01	62	2.0	
10-02	62	1.6	0.4
10-03	62	1.4	0.6

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Concentrate composition	Glyphosate g a.e./l	Weight %	
		Hetoxol CS-25	Ethoquad 18/25
10-04	62	1.0	1.0
10-05	62	0.6	1.4
10-06	62		2.0

Glyphosate concentration in all compositions was approximately 6% a.e. by weight.

- 5 Velvetleaf (*Abutilon theophrasti*, ABUTH) plants were grown and treated by the standard procedures given above, except that 6 replicate pots were subjected to each treatment, applied in two sets of three pots. Applications of plant treatment compositions were made 23 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application.

- 10 MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for all replicates of each treatment, are shown in Table 10b.

Table 10b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition ABUTH
MON 0139	100	1
	200	10
	300	29
	400	49
	500	77
Roundup® Ultra	100	10
	200	60
	300	82
	400	86
	500	93
10-01	100	42
	200	78
	300	88
	400	95
	500	98
10-02	100	53
	200	83
	300	96
	400	98
	500	98

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition
		ABUTH
10-03	100	52
	200	82
	300	92
	400	98
	500	99
10-04	100	56
	200	84
	300	96
	400	98
	500	98
10-05	100	49
	200	82
	300	96
	400	97
	500	98
10-06	100	7
	200	55
	300	75
	400	92
	500	98

Compositions 10-02 to 10-05 of the present invention, containing mixtures of an alkylether surfactant (Hetoxol™ CS-25) and an amine surfactant (Ethoquad™ 18/25) exhibited greater herbicidal effectiveness than either composition 10-01 (the alkylether alone) or 10-06 (the amine alone) at the same total surfactant concentration.

Example 11

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 11a.

Compositions 11-01 to 11-04 were prepared by adding to water, in the following sequence, the alkylether surfactant Plurafac™ A-38, then soybean lecithin (95% phospholipids, Avanti), then the amine surfactant MON 0818, then butyl stearate. If a coupling agent was included, it was added first to the Plurafac™ A-38 before other ingredients were added. The resulting mixture was fan mixed for 10 minutes and then placed in a shaker bath at 50°C for 30 minutes. Finally glyphosate IPA salt in the form of MON 0139 was added and the composition thoroughly mixed.

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Table 11a

Conc. comp.	Glyphosate g a.e./l	Weight %					Coupling agent
		Lecithin	Butyl stearate	Plurafac A-38	MON 0818	Coupling agent	
11-01	220	3.0	1.5	3.0	3.0		none
11-02	357	5.0	2.5	4.5	4.5	2.5	ethanol
11-03	357	5.0	2.5	4.5	4.5	1.0	urea
11-04	347	5.0	2.5	4.5	4.5	1.0	N(Bu) ₄ OH*

* tetrabutylammonium hydroxide

Glyphosate concentration in composition 11-01 was approximately 20% a.e. by weight, in compositions 11-02 to 11-04 was approximately 30% a.e. by weight.

- 5 Velvetleaf (*Abutilon theophrasti*, ABUTH) plants were grown and treated by the standard procedures given above, except that 6 replicate pots were subjected to each treatment, applied in two sets of three pots. Applications of plant treatment compositions were made 17 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application.

- 10 MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for all replicates of each treatment, are shown in Table 11b.

Table 11b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition
		ABUTH
MON 0139	100	22
	200	38
	400	74
	600	89
	800	92
Roundup® Ultra	100	46
	200	69
	400	96
	600	98
	800	100
11-01	100	66
	200	77
	400	96
	600	98
	800	100

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition
		ABUTH
11-02	100	62
	200	77
	400	97
	600	99
	800	100
11-03	100	65
	200	77
	400	96
	600	99
	800	99
11-04	100	58
	200	78
	400	97
	600	97
	800	100

Example 12

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 12a.

- 5
- Compositions 12-01 to 12-03 were prepared by the following procedure. Soybean lecithin (95% phospholipids, Avanti) was added to water and fan-mixed with a Variac mixer, set at 30% of maximum voltage, for about 10 minutes, to hydrate the lecithin. To the hydrated lecithin in water were then added the alkylether surfactant Plurafac™ A-38, the amine surfactant MON 0818, butyl stearate, a coupling agent and
- 10
- glyphosate IPA salt in the form of MON 0139. The resulting mixture was first agitated by hand shaking and then mixed with a Turrax mixer at 20,000 rpm for about 8 minutes.

Table 12a

Conc. comp.	Glyphosate g a.e./l	Weight %					Coupling agent
		Lecithin	Butyl stearate	Plurafac A-38	MON 0818	Coupling agent	
12-01	354	5.0	2.5	4.5	4.5	0.5	DMSO
12-02	330	4.0	2.0	6.5	6.0	1.0	butanol
12-03	353	4.0	2.0	8.5	4.5	1.0	butanol

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- Glyphosate concentration in each composition was approximately 30% a.e. by

weight.

Velvetleaf (*Abutilon theophrasti*, ABUTH) plants were grown and treated by the standard procedures given above, except that 6 replicate pots were subjected to each treatment, applied in two sets of three pots. One set of three pots for each treatment was subjected to simulated rain, using an overhead irrigator, in the amount of 6 mm, one hour after application of plant treatment compositions. Applications of plant treatment compositions were made 18 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application.

MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for all replicates of each treatment, are shown in Table 12b.

Table 12b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition, ABUTH	
		no rain	rain
MON 0139	250	53	27
	500	82	42
	750	96	62
Roundup® Ultra	250	88	47
	500	99	70
	750	100	87
12-01	250	97	66
	500	99	83
	750	100	95
12-02	250	97	77
	500	99	90
	750	100	97
12-03	250	95	73
	500	100	86
	750	100	96

Compositions 12-01 to 12-03 are representative of an embodiment of the present invention in which an alkylether and an amine surfactant are coformulated with glyphosate in such a way that the glyphosate is believed strongly associated with or entrapped by supramolecular aggregates. Compositions 12-01 to 12-03 in the greenhouse test of this Example not only exhibited significantly enhanced herbicidal effectiveness over that provided by the commercial standard Roundup® Ultra in the absence of rain; in addition, they showed greatly enhanced rainfastness.

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237Example 13

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 13a.

- Composition 13-01 contained a colloidal particulate silica, Aerosil™ 380 of Degussa, and was prepared as follows. The required amount of Aerosil™ 380 was suspended in a concentrated glyphosate IPA salt solution (MON 0139) and agitated with cooling to ensure homogeneity of the resulting glyphosate/silica mixture. The alkylether surfactant Plurafac™ A-38 was heated to bring it into a flowable condition and was then added in the required amount by weight to the glyphosate/silica mixture.
- The required amount of water was then added to bring the concentration of glyphosate and other ingredients to the desired level. The composition was finally subjected to high-shear mixing using a Silverson L4RT-A mixer fitted with a medium emulsor screen, operated for 3 minutes at 7,000 rpm. Compositions 13-02 to 13-05 were prepared by the procedure of Example 12.

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Table 13a

Conc. comp.	Glyphosate g a.e./l	Weight %					Other ingredient
		Lecithin	Butyl stearate	Plurafac A-38	MON 0818	Other	
13-01	357			10.0		1.25	Aerosil 380
13-02	347	4.0	2.0	6.5	6.5	1.0	butanol
13-03	349	4.0	2.0	8.5	4.5	1.0	butanol
13-04	335	4.0	2.0	10.0	3.0	1.0	butanol
13-05	357	5.0	2.0	4.5	4.5	1.0	DMSO

Glyphosate concentration in each composition was approximately 30% a.e. by weight.

- Velvetleaf (*Abutilon theophrasti*, ABUTH) plants were grown and treated by the standard procedures given above, except that 6 replicate pots were subjected to each treatment, applied in two sets of three pots. One set of three pots for each treatment was subjected to simulated rain, using an overhead irrigator, in the amount of 6 mm, one hour after application of plant treatment compositions. Applications of plant treatment compositions were made 22 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application.

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MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for all replicates of each treatment, are shown in Table 13b.

Table 13b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition, ABUTH	
		no rain	rain
MON 0139	300	68	10
	600	93	35
	900	97	60
Roundup® Ultra	300	78	57
	600	98	70
	900	100	73
13-01	300	98	70
	600	99	86
	900	100	98
13-02	300	97	67
	600	99	93
	900	100	93
13-03	300	98	72
	600	100	82
	900	100	97
13-04	300	98	70
	600	99	85
	900	100	93
13-05	300	100	68
	600	98	94
	900	100	98

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Compositions 13-02 to 13-05 are representative of an embodiment of the present invention in which an alkylether and an amine surfactant are coformulated with glyphosate in such a way that the glyphosate is believed strongly associated with or entrapped by supramolecular aggregates. Compositions 13-02 to 13-05 in the greenhouse test of this Example not only exhibited significantly enhanced herbicidal effectiveness over that provided by the commercial standard Roundup® Ultra in the absence of rain; in addition, they showed greatly enhanced rainfastness. Excellent herbicidal effectiveness and rainfastness were also exhibited by composition 13-01, which contains an alkylether surfactant but no amine surfactant.

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235Example 14

Aqueous concentrate compositions were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 14a.

Composition 14-01 was prepared by adding colloidal particulate silica (a blend of Aerosil™ 380 and Aerosil™ MOX-80 of Degussa, in a 9:1 weight ratio) to glyphosate IPA salt solution (MON 0139) and mixing with a Turrax mixer on ice at 20,500 rpm for about 8 minutes to form a glyphosate/silica mixture. The alkylether surfactant Plurafac™ A-38 of BASF was then added to the glyphosate/silica mixture and the resulting composition was mixed with a Turrax mixer on ice at 20,500 rpm for a further 5 minutes. Compositions 14-02 to 14-05 were prepared by the procedure of Example 12.

Table 14a

Conc. comp.	Glyphosate g a.e./l	Weight %					Other ingredient
		Lecithin	Butyl stearate	Plurafac A-38	MON 0818	Other	
14-01	472			13.5		2.5	colloidal silica
14-02	351	5.0	2.5	4.5	4.5	0.5	DMSO
14-03	354	6.0	2.5	6.5	6.5	0.5	DMSO
14-04	335	5.0	2.5	6.5	4.5 ¹	0.5	butanol
14-05	357	5.0	2.5	6.5 ²	8.5	1.0	urea

¹ MON 0818 replaced in this composition by Ethoquad™ 18/25 of Akzo

² Plurafac™ A-38 replaced in this composition by Hetoxol™ CS-25 of Heterene

Glyphosate concentration in composition 14-01 was approximately 40% a.e. by weight. Glyphosate concentration in compositions 14-02 to 14-05 was approximately 30% a.e. by weight.

Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above, except that 6 replicate pots of each species were subjected to each treatment, applied in two sets of three pots. Applications of plant treatment compositions were made 18 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 15 days after application.

MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for each treatment, are shown in Table 14b.

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Table 14b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
MON 0139	100	1	4
	200	5	32
	300	45	45
	400	56	50
	500	2	59
Roundup® Ultra	100	31	44
	200	74	56
	300	88	72
	400	97	77
	500	99	86
14-01	100	53	43
	200	74	48
	300	88	64
	400	94	78
	500	99	86
14-02	100	45	40
	200	73	52
	300	92	65
	400	97	77
	500	99	89
14-03	100	55	37
	200	79	58
	300	94	72
	400	95	74
	500	99	94
14-04	100	57	41
	200	81	61
	300	93	76
	400	96	80
	500	99	88
14-05	100	57	43
	200	81	60
	300	94	79
	400	98	82
	500	99	91

Example 15

- Aqueous concentrate compositions 15-01 to 15-05 were prepared identically to
- 5 compositions 14-01 to 14-05 respectively, as shown in Table 15a.

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Table 15a

Conc. comp.	Glyphosate g a.e./l	Weight %					Other ingredient
		Lecithin	Butyl stearate	Plurafac A-38	MON 0818	Other	
15-01	472			13.5		2.5	colloidal silica
15-02	351	5.0	2.5	4.5	4.5	0.5	DMSO
15-03	354	6.0	2.5	6.5	6.5	0.5	DMSO
15-04	335	5.0	2.5	6.5	4.5 ¹	0.5	butanol
15-05	357	5.0	2.5	6.5 ²	8.5	1.0	urea

¹ MON 0818 replaced in this composition by Ethoquad™ 18/25 of Akzo² Plurafac™ A-38 replaced in this composition by Hetoxol™ CS-25 of Heterene

- Velvetleaf (*Abutilon theophrasti*, ABUTH), morningglory (*Ipomoea* sp., IPOSS) and prickly sida (*Sida spinosa*, SIDSP) plants were grown and treated by the standard procedures given above, except that 6 replicate pots of each species were subjected to each treatment, applied in two sets of three pots. Applications of plant treatment compositions were made 13 days after planting IPOSS, 20 days after planting ABUTH and 24 days after planting SIDSP, and evaluation of herbicidal effectiveness was done 15 days after application.

MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Results, averaged for each treatment, are shown in Table 15b.

Table 15b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition		
		ABUTH	IPOSS	SIDSP
MON 0139	100	1	0	13
	200	29	17	30
	400	62	63	58
	600	70	68	68
	800	81	79	73
Roundup® Ultra	100	46	6	45
	200	75	60	68
	400	90	75	84
	600	98	84	83
	800	99	94	92
15-01	100	71	11	8
	200	81	46	78
	400	93	71	84
	600	98	82	90
	800	99	91	88

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition		
		ABUTH	IPOSS	SIDSP
15-02	100	61	5	48
	200	81	67	66
	400	94	81	82
	600	97	91	88
	800	98	94	91
15-03	100	66	8	51
	200	83	59	69
	400	94	75	84
	600	98	85	90
	800	99	92	93
15-04	100	71	20	57
	200	83	69	77
	400	96	81	85
	600	98	92	92
	800	99	98	94
15-05	100	68	17	68
	200	84	54	78
	400	97	81	86
	600	98	88	92
	800	99	95	94

Example 16

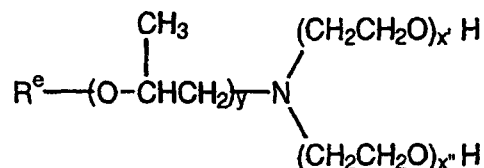
Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt and excipient ingredients as shown in Table 16a.

- 5 Compositions 16-01 to 16-13 were all prepared by the following procedure. The selected surfactant or surfactants were first heated if necessary to bring them to a flowable state. Dry ammonium glyphosate powder (MON 8750 of Monsanto) was mixed with a small amount of water (typically about 5 g per 100 g of all other ingredients) and with the selected surfactant(s) to make a wet mix which was kneaded
- 10 until a homogeneous smooth dough-like paste was produced. This paste was transferred to a radial extruder fitted with screens having 1 mm orifices and extruded through these orifices. The resulting strands of extrudate broke spontaneously to form short cylindrical granules which were then dried in a fluid bed dryer.

- 15 Surfactants used in the compositions of this Example were the alkylether surfactant Plurafac™ A-38 of BASF and amine surfactants A, B and C, respectively polyoxyethylene (20) tallowamine, polyoxyethylene (10) N-methyl tallowammonium

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chloride (Ethoquad™ T/20 of Akzo), and a surfactant of formula



where R^e is C₁₂₋₁₅ alkyl, y is 2 and x' + x'' is an average number of about 5, as disclosed in U.S. Patent No. 5,750,468.

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Table 16a

Granule composition	Weight %				
	Glyphosate a.e.	Plurafac A-38	amine surfactant A	amine surfactant B	amine surfactant C
16-01	68.0	21.4			
16-02	68.0	16.0	5.4		
16-03	68.0	10.7	10.7		
16-04	68.0	5.5	16.0		
16-05	68.0		21.4		
16-06	68.0	16.0		5.4	
16-07	68.0	10.7		10.7	
16-08	68.0	5.5		16.0	
16-09	68.0			21.4	
16-10	68.0	16.0			5.4
16-11	68.0	10.7			10.7
16-12	68.0	5.5			16.0
16-13	68.0				21.4

Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 17 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 20 days after application.

Roundup® Ultra was diluted and applied as a comparative treatment. Results, averaged for all replicates of each treatment, are shown in Table 16b.

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Table 16b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Roundup® Ultra	50	3	10
	100	50	53
	200	85	88
	300	90	100
	500	100	97
16-01	50	33	5
	100	70	53
	200	93	83
	300	98	92
	500	100	100
16-02	50	30	13
	100	70	67
	200	93	87
	300	100	96
	500	100	99
16-03	50	23	27
	100	68	70
	200	98	89
	300	99	95
	500	100	99
16-04	50	10	33
	100	67	73
	200	98	93
	300	99	99
	500	100	98
16-05	50	0	20
	100	33	57
	200	87	82
	300	95	93
	500	100	97
16-06	50	42	28
	100	72	60
	200	94	83
	300	100	95
	500	100	98
16-07	50	38	45
	100	75	70
	200	99	85
	300	100	99
	500	100	100

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
16-08	50	30	47
	100	75	70
	200	99	85
	300	99	99
	500	100	94
16-09	50	0	17
	100	33	67
	200	87	83
	300	98	94
	500	100	92
16-10	50	32	40
	100	70	57
	200	94	83
	300	100	95
	500	100	100
16-11	50	17	43
	100	67	65
	200	97	97
	300	100	97
	500	100	98
16-12	50	10	30
	100	60	65
	200	88	85
	300	98	90
	500	100	95
16-13	50	0	20
	100	10	55
	200	65	83
	300	95	83
	500	100	100

Clear evidence of a synergistic interaction between the alkylether surfactant and the amine surfactant component of the compositions of this Example was seen. In the case of amine surfactants A and C, the synergism was evident on ECHCF; in the case of amine surfactant B, the synergism was evident on both ABUTH and ECHCF.

Example 17

Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt and excipient ingredients as shown in Table 17a.

Compositions 17-01 to 17-10 were prepared by the procedure described in

Example 16. Compositions 17-06 to 17-10 contained, in addition to glyphosate ammonium salt and surfactant(s), ammonium sulfate. This was added to the wet mix during kneading.

Table 17a

Granule composition	Weight %			
	Glyphosate a.e.	Plurafac A-38	amine surfactant A	ammonium sulfate
17-01	68.0	21.0		
17-02	68.0	15.8	5.2	
17-03	68.0	10.5	10.5	
17-04	68.0	5.2	15.8	
17-05	68.0		21.0	
17-06	34.0	10.3		50.0
17-07	34.0	7.8	2.5	50.0
17-08	34.0	5.2	5.2	50.0
17-09	34.0	2.5	7.8	50.0
17-10	34.0		10.3	50.0

5

Filaree (*Erodium* sp., EROSS) and annual bluegrass (*Poa annua*, POAAN) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 41 days after planting EROSS and POAAN, and evaluation of herbicidal effectiveness was done 21 days after

10 application.

Roundup® Ultra was diluted and applied as a comparative treatment. Results, averaged for all replicates of each treatment, are shown in Table 17b.

Table 17b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		EROSS	POAAN
Roundup® Ultra	400	50	30
	600	75	43
	800	88	60
	1000	97	75
17-01	400	77	40
	600	87	63
	800	88	68
	1000	95	70

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		EROSS	POAAN
17-02	400	70	22
	600	85	42
	800	95	53
	1000	90	75
17-03	400	78	30
	600	90	45
	800	93	65
	1000	95	68
17-04	400	72	37
	600	88	53
	800	93	53
	1000	93	67
17-05	400	52	28
	600	67	42
	800	83	42
	1000	95	63
17-06	400	68	38
	600	90	45
	800	92	48
	1000	97	62
17-07	400	80	40
	600	88	45
	800	97	62
	1000	95	68
17-08	400	82	48
	600	92	63
	800	98	60
	1000	97	78
17-09	400	73	53
	600	88	60
	800	90	63
	1000	97	88
17-10	400	55	37
	600	80	48
	800	85	48
	1000	92	62

A synergistic interaction between the alkylether surfactant and the amine surfactant component of the compositions of this Example was evident on EPOSS and POAAN for compositions 17-07 to 17-09 containing ammonium sulfate.

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Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt and excipient ingredients as shown in Table 18a.

Compositions 18-01 to 18-05 were prepared by the procedure described in

- 5 Example 16 and were identical to compositions 17-01 to 17-05 respectively.

Table 18a

Granule composition	Weight %			
	Glyphosate a.e.	Plurafac A-38	amine surfactant A	ammonium sulfate
18-01	68.0	21.0		
18-02	68.0	15.8	5.2	
18-03	68.0	10.5	10.5	
18-04	68.0	5.2	15.8	
18-05	68.0		21.0	

- 10 Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 18 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 17 days after application.

Roundup® Ultra was diluted and applied as a comparative treatment. Results, averaged for all replicates of each treatment, are shown in Table 18b.

15

Table 18b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Roundup® Ultra	100	18	35
	200	83	70
	300	90	82
	400	98	90
	600	98	90
18-01	100	53	35
	200	85	73
	300	97	85
	400	100	94
	600	100	98

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
18-02	100	68	47
	200	94	77
	300	99	87
	400	100	95
	600	100	99
18-03	100	60	50
	200	95	80
	300	97	93
	400	100	95
	600	100	98
18-04	100	40	50
	200	85	78
	300	98	90
	400	99	95
	600	100	99
18-05	100	10	27
	200	78	58
	300	83	77
	400	90	87
	600	99	93

A synergistic interaction between the alkylether surfactant and the amine surfactant component of the compositions of this Example was evident on ABUTH and ECHCF.

5 Example 19

Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt and excipient ingredients as shown in Table 19a.

Compositions 19-01 to 19-10 were prepared by the procedure described in Example 16. Compositions 19-06 to 19-10 contained, in addition to glyphosate ammonium salt and surfactant(s), ammonium sulfate. This was added to the wet mix during kneading. Compositions 19-01 to 19-10 were identical to compositions 17-01 to 17-10 respectively.

Table 19a

Granule composition	Weight %			
	Glyphosate a.e.	Plurafac A-38	amine surfactant A	ammonium sulfate
19-01	68.0	21.0		

Granule composition	Weight %			
	Glyphosate a.e.	Plurafac A-38	amine surfactant A	ammonium sulfate
19-02	68.0	15.8	5.2	
19-03	68.0	10.5	10.5	
19-04	68.0	5.2	15.8	
19-05	68.0		21.0	
19-06	34.0	10.3		50.0
19-07	34.0	7.8	2.5	50.0
19-08	34.0	5.2	5.2	50.0
19-09	34.0	2.5	7.8	50.0
19-10	34.0		10.3	50.0

- Indian mustard (*Brassica juncea*, BRSJU) and downy brome (*Bromus tectorum*, BROTE) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 25 days after planting BRSJU and BROTE, and evaluation of herbicidal effectiveness was done 18 days after application.

Roundup® Ultra was diluted and applied as a comparative treatment. Results, averaged for all replicates of each treatment, are shown in Table 19b.

Table 19b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		BRSJU	BROTE
Roundup® Ultra	300	48	90
	400	62	93
	600	65	97
	800	88	99
19-01	300	42	52
	400	60	67
	600	80	85
	800	83	90
19-02	300	43	53
	400	75	88
	600	77	98
	800	88	99
19-03	300	50	82
	400	82	93
	600	90	97
	800	92	100

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		BRSJU	BROTE
19-04	300	52	80
	400	75	94
	600	85	98
	800	92	100
19-05	300	52	63
	400	68	90
	600	87	98
	800	87	98
19-06	300	57	65
	400	58	85
	600	78	93
	800	85	99
19-07	300	47	57
	400	73	83
	600	83	97
	800	90	100
19-08	300	52	88
	400	82	94
	600	85	98
	800	92	99
19-09	300	62	80
	400	78	87
	600	92	99
	800	90	100
19-10	300	47	60
	400	63	87
	600	83	97
	800	92	99

A synergistic interaction between the alkylether surfactant and the amine surfactant component of the compositions of this Example was evident on BRSJU and BROTE.

5 Example 20

Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt and excipient ingredients as shown in Table 20a.

Compositions 20-01 to 20-04 were prepared by the procedure described in Example 16. These compositions contained, in addition to glyphosate ammonium salt and surfactant(s), polyethylene glycol having an average molecular weight of about

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8000 (PEG 8000). This was heated to a flowable state and added to the wet mix during kneading. Surfactants used in the compositions of this Example were the following alkylether surfactants: polyoxyethylene stearylether having an average of about 10 oxyethylene units per molecule (steareth-10, Brij™ 76 of ICI), and

5 polyoxyethylene stearylether having an average of about 20 oxyethylene units per molecule (steareth-20, Emthox™ 5888 of Henkel). Compositions included for comparative purposes contained other nonionic surfactants: polyoxyethylene dodecylphenol having an average of about 10 oxyethylene units per molecule (POE (10) dodecylphenol), or polyoxyethylene sorbitan laurylester having an average of

10 about 20 oxyethylene units per molecule (Tween™ 20 of ICI). The amine surfactant in all compositions was either polyoxyethylene N-methyl tallowammonium chloride having an average of about 15 oxyethylene units per molecule (Ethoquad™ T/25 of Akzo) or polyoxyethylene N-methyl stearyl ammonium chloride having an average of about 15 oxyethylene units per molecule (Ethoquad™ 18/25 of Akzo). It will be

15 recognized that these two amine surfactants are very similar, differing only in the hydrogenation of the tallowalkyl group to provide a stearyl moiety in Ethoquad™ 18/25.

Table 20a

Granule composition	Weight %				Nonionic surfactant
	Glyphosate a.e.	nonionic surfactant	Ethoquad T/25	PEG 8000	
20-01	64.5	10.0	20.0	10.0	Tween 20
20-02	64.5	10.0	20.0 ¹	10.0	POE (10) dodecylphenol
20-03	64.5	10.0	20.0	10.0	steareth-10
20-04	64.5	10.0	20.0	10.0	steareth-20

¹ Ethoquad™ 18/25 in place of Ethoquad™ T/25

20 Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 18 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 17

days after application.

25 Roundup® Ultra was diluted and applied as a comparative treatment. Also included as a comparative treatment was composition 16-05 of Example 16. Results,

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averaged for all replicates of each treatment, are shown in Table 20b.

Table 20b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Roundup® Ultra	100	20	30
	200	78	65
	300	97	72
	500	100	96
16-05	100	5	30
	200	63	63
	300	85	70
	500	100	77
20-01	100	2	43
	200	72	67
	300	96	73
	500	100	82
20-02	100	5	13
	200	67	68
	300	85	75
	500	99	77
20-03	100	12	40
	200	88	67
	300	96	73
	500	99	92
20-04	100	75	45
	200	98	73
	300	99	77
	500	100	90

- 5 Compositions 20-03 and 20-04 of the invention exhibited greater herbicidal effectiveness than compositions 20-01 or 20-02, especially on ABUTH. The superior herbicidal effectiveness of composition 20-04, containing the alkylether surfactant steareth-20 and the amine surfactant Ethoquad™ T/25, was particularly marked.

Example 21

- 10 Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt and excipient ingredients as shown in Table 21a.

Compositions 21-01, 21-03 and 21-04 were prepared by the procedure described in Example 16 and were identical to compositions 20-01, 20-03 and 20-04 respectively.

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Table 21a

Granule composition	Weight %				Nonionic surfactant
	Glyphosate a.e.	nonionic surfactant	Ethoquad T/25	PEG 8000	
21-01	64.5	10.0	20.0	10.0	Tween 20
21-03	64.5	10.0	20.0	10.0	steareth-10
21-04	64.5	10.0	20.0	10.0	steareth-20

- Kochia (*Kochia scoparia*, KCHSC), downy brome (*Bromus tectorum*, BROTE) and winter wheat (*Triticum aestivum*, TRZAW) plants were grown and treated by the standard procedures given above, except that six replicate pots of KCHSC were subjected to each treatment. Applications of plant treatment compositions were made 35 days after planting KCHSC, 27 days after planting BROTE and 14 days after planting TRZAW. Evaluation of herbicidal effectiveness was done 15 days after application on KCHSC and 21 days after application on BROTE and TRZAW.

Roundup® Ultra was diluted and applied as a comparative treatment. Also included as a comparative treatment was composition 16-05 of Example 16. Results, averaged for all replicates of each treatment, are shown in Table 21b.

Table 21b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition		
		KCHSC	BROTE	TRZAW
Roundup® Ultra	100	37	46	33
	200	83	86	76
	400	99	92	97
	600	100	99	97
16-05	100	36	12	50
	200	82	63	81
	400	98	82	99
	600	100	100	100
21-01	100	35	28	59
	200	84	74	87
	400	99	92	100
	600	100	98	100
21-03	100	43	36	56
	200	77	90	94
	400	96	99	98
	600	100	100	99

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition		
		KCHSC	BROTE	TRZAW
21-04	100	44	43	37
	200	92	73	91
	400	100	99	100
	600	100	100	100

Example 22

Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt and excipient ingredients as shown in Table 22a.

- 5 Compositions 22-01 to 22-17 were prepared by the procedure described in Example 16. All compositions contained amine surfactant A of Example 16. Alkylether surfactants used in the compositions of this Example were polyoxyethylene (C₁₂ alkyl)ether having an average of about 4 oxyethylene units per molecule (laureth-4, Brij™ 30 of ICI), polyoxyethylene (C₁₂ alkyl)ether having an average of about 12
- 10 oxyethylene units per molecule (laureth-12, Trycol™ 5967 of Henkel), polyoxyethylene (C₁₂ alkyl)ether having an average of about 23 oxyethylene units per molecule (laureth-23, Trycol™ 5964 of Henkel), polyoxyethylene (C₁₈ alkyl)ether having an average of about 5 oxyethylene units per molecule (steareth-5),
- 15 polyoxyethylene (C₁₈ alkyl)ether having an average of about 10 oxyethylene units per molecule (steareth-12, Brij™ 76 of ICI), polyoxyethylene (C₁₈ alkyl)ether having an average of about 20 oxyethylene units per molecule (steareth-20, Emthox™ 5888 of Henkel), polyoxyethylene (C₁₈ alkyl)ether having an average of about 30 oxyethylene
- 20 units per molecule (steareth-30, STA-30 of Heterene), and polyoxyethylene (C₁₆₋₁₈ alkyl)ether having an average of about 23 oxyethylene units per molecule (cetareth-23, Plurafac™ A-38 of BASF).

Table 22a

Granule composition	Weight %			Alkylether surfactant
	Glyphosate a.e.	alkylether surfactant	amine surfactant A	
22-01	68.0	21.4		laureth-4
22-02	68.0	10.7	10.7	laureth-4
22-03	68.0	21.4		laureth-12
22-04	68.0	10.7	10.7	laureth-12
22-05	68.0	21.4		laureth-23

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Granule composition	Weight %			Alkylether surfactant
	Glyphosate a.e.	alkylether surfactant	amine surfactant A	
22-06	68.0	10.7	10.7	laureth-23
22-07	68.0	21.4		steareth-5
22-08	68.0	10.7	10.7	steareth-5
22-09	68.0	21.4		steareth-10
22-10	68.0	10.7	10.7	steareth-10
22-11	68.0	21.4		steareth-20
22-12	68.0	10.7	10.7	steareth-20
22-13	68.0	21.4		steareth-30
22-14	68.0	10.7	10.7	steareth-30
22-15	68.0	21.4		ceteareth-23
22-16	68.0	10.7	10.7	ceteareth-23
22-17	68.0		21.4	none

Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 17 days after planting ABUTH and ECHCF, and evaluation of herbicidal effectiveness was done 15 days after application.

Roundup® Ultra was diluted and applied as a comparative treatment. Results, averaged for all replicates of each treatment, are shown in Table 22b. Where a blend of alkylether and amine surfactants elicited herbicidal effectiveness that was at least equal to the better of the alkylether or amine surfactant alone at the same total surfactant concentration, the average percent inhibition *nn* for that blend is highlighted thus: ** *nn* **.

Table 22b

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
Roundup® Ultra	100	50	28
	200	85	40
	300	99	57
	500	100	89
22-01	100	0	3
	200	10	8
	300	70	33
	500	80	45

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Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
22-02	100	0	** 37 **
	200	63	22
	300	80	55
	500	90	** 90 **
22-03	100	0	30
	200	60	38
	300	82	53
	500	90	90
22-04	100	** 27 **	** 33 **
	200	78	40
	300	** 92 **	55
	500	98	** 93 **
22-05	100	5	33
	200	73	43
	300	90	57
	500	95	92
22-06	100	2	** 35 **
	200	73	42
	300	87	** 73 **
	500	94	** 100 **
22-07	100	0	8
	200	8	27
	300	32	43
	500	55	47
22-08	100	3	** 37 **
	200	** 85 **	** 48 **
	300	** 96 **	** 70 **
	500	** 99 **	** 95 **
22-09	100	5	20
	200	78	32
	300	88	47
	500	92	97
22-10	100	** 55 **	** 38 **
	200	** 83 **	** 47 **
	300	** 93 **	** 73 **
	500	** 99 **	** 100 **
22-11	100	53	35
	200	87	47
	300	96	75
	500	99	98

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25A

Concentrate composition	Glyphosate rate g a.e./ha	% Inhibition	
		ABUTH	ECHCF
22-12	100	** 78 **	** 35 **
	200	** 93 **	45
	300	** 98 **	** 87 **
	500	** 100 **	97
22-13	100	73	30
	200	87	38
	300	97	57
	500	99	95
22-14	100	** 77 **	** 33 **
	200	** 87 **	** 47 **
	300	** 97 **	** 62 **
	500	** 99 **	** 95 **
22-15	100	75	28
	200	89	45
	300	98	77
	500	100	95
22-16	100	** 77 **	** 35 **
	200	88	** 47 **
	300	** 98 **	** 88 **
	500	99	** 99 **
22-17	100	13	27
	200	80	42
	300	83	60
	500	99	73

It will be noted from Table 22b that where the alkylether surfactant had a relatively short-chain (C_{12}) alkyl moiety, as in compositions 22-01 to 22-06, some sporadic instances were observed of the blend with amine surfactant A eliciting herbicidal effectiveness at least equal to the better of the alkylether or the amine. With longer-chain (C_{16-18}) alkylethers, however, equal to superior performance of the blend with amine surfactant A (by comparison with either surfactant alone) was the rule rather than the exception. In some instances there was evidence of a very dramatic synergistic interaction. The greatest degree of herbicidal effectiveness was obtained with C_{16-18} alkylethers having 20 or more oxyethylene units per molecule.

Example 23

Aqueous concentrate compositions 23-01 and 23-02 were prepared containing glyphosate IPA salt and excipient ingredients as shown in Table 23a. Neodol™ 25-9

of Shell is a polyoxyethylene C₁₃ alkylether surfactant having an average of about 9 oxyethylene units per molecule. Brij™ 56 of ICI is a polyoxyethylene cetyether surfactant having an average of about 10 oxyethylene units per molecule.

Rhodaquat™ DAET of Rhodia is a quaternary ditallowalkylammonium sulfate

- 5 surfactant having no oxyethylene units. Ethoquad™ T/25 of Akzo is a polyoxyethylene quaternary tallowalkyltrimethylammonium chloride surfactant having an average of about 15 oxyethylene units per molecule. Compositions 23-01 and 23-02 were prepared by mixing the ingredients with heating and agitation until the resulting mixture was homogeneous. Composition 23-01 was included for
- 10 comparative purposes only.

Table 23a

Concentrate composition	Glyphosate g a.e./l	Weight %			
		Neodol 25-9	Brij 56	Rhodaquat DAET	Ethoquad T/25
23-01	345	7.5		7.5	
23-02	349		7.5		7.5

Glyphosate concentration in each of compositions 23-01 and 23-02 was approximately 30% a.e. by weight.

- 15 Velvetleaf (*Abutilon theophrasti*, ABUTH) plants were grown and treated by the standard procedures given above, except that 6 replicate pots were subjected to each treatment, applied in two sets of three pots. One set of three pots for each treatment was subjected to simulated rain, using an overhead irrigator, in the amount of 6 mm, one hour after application of plant treatment compositions. Applications of
- 20 plant treatment compositions were made 18 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application.

- In addition to compositions 23-01 and 23-02, composition 12-01 of Example 12 was included in the test of this Example. MON 0139 and Roundup® Ultra were diluted and applied as comparative treatments. Also included as a comparative
- 25 treatment was MON 0139, diluted and applied in tank-mixture with the organosilicone surfactant Silwet™ L-77 of OSi Specialties Group of Witco Corp., at 0.5% by volume. Results, averaged for all replicates of each treatment, are shown in Table 23b.

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Table 23b

Composition	Glyphosate rate g a.e./ha	% Inhibition, ABUTH	
		no rain	rain
MON 0139	250	19	0
	500	63	0
	750	78	9
Roundup® Ultra	250	78	43
	500	98	50
	750	98	69
MON 0139 + Silwet L-77	250	75	69
	500	94	95
	750	98	97
12-01	250	82	53
	500	98	80
	750	99	80
23-01	250	60	10
	500	92	46
	750	98	62
23-02	250	84	68
	500	98	94
	750	98	98

Composition 23-02 of the present invention exhibited a remarkably high degree of rainfastness in this test, equal to that of the rainfastness standard MON 0139 + Silwet™ L-77. Composition 12-01 of the present invention also exhibited rainfastness markedly superior to that of the commercial standard Roundup® Ultra. Comparative composition 23-01 showed very poor rainfastness.

The test of this Example was repeated. Applications of plant treatment compositions were again made 18 days after planting ABUTH, and evaluation of herbicidal effectiveness was done 14 days after application. Results, averaged for all replicates of each treatment, are shown in Table 23c.

Table 23c

Composition	Glyphosate rate g a.e./ha	% Inhibition, ABUTH	
		no rain	rain
MON 0139	250	2	0
	500	73	0
	750	81	2

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Composition	Glyphosate rate g a.e./ha	% Inhibition, ABUTH	
		no rain	rain
Roundup® Ultra	250	87	53
	500	98	65
	750	98	67
MON 0139 + Silwet L-77	250	88	93
	500	99	98
	750	99	99
12-01	250	78	55
	500	97	81
	750	99	91
23-01	250	84	12
	500	98	63
	750	87	63
23-02	250	87	67
	500	98	94
	750	99	96

Results of this repeat test were consistent with those of the first test shown in Table 23b.

Example 24

- 5 Samples of seven liquid aqueous concentrate compositions 24-01 to 24-07 were examined by proton NMR spectroscopy using the pulse field gradient method of Wu *et al.*, *op. cit.* to measure diffusion rates. The excipient ingredients of the compositions were as detailed in Table 24. Each composition contained glyphosate isopropylammonium salt at a concentration of 30% a.e. by weight. Compositions
- 10 were prepared by procedures hereinabove described. Three separate preparations of composition 24-04 and two separate preparations of composition 24-05 were studied. The alkylether surfactant was Plurafac™ A-38 of BASF in all compositions except 24-01, in which the very similar Hetoxol™ CS of Heterene was used. The amine surfactant in all compositions was MON 0818 of Monsanto. The coupling agent was
- 15 DMSO in all compositions except 24-01, wherein the DMSO was replaced by urea.

Table 24

Concentrate composition	Weight %				
	alkylether surfactant	amine surfactant	soybean lecithin	butyl stearate	coupling agent
24-01	4.5	8.5	5.0	2.5	1.0

100
255
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Concentrate composition	Weight %				
	alkylether surfactant	amine surfactant	soybean lecithin	butyl stearate	coupling agent
24-02	6.0	6.0	6.0	2.5	0.5
24-03	4.5	6.0	6.0	2.5	0.5
24-04	4.5	4.5	5.0	2.5	0.5
24-05	4.5	4.5	6.0	3.0	0.5
24-06	4.5	4.5	6.0	2.5	0.5
24-07	6.0	4.5	6.0	2.5	0.5

A 200-500 μ l sample of each composition was placed in an NMR tube for diffusion measurement using a Nalorac diffusion probe having a diffusion coil capable of producing a linear field gradient across the sample of about 250 gauss/cm in response to a 20 amp current pulse. The current pulse was generated by a Performa gradient driver inside the console of a Varian Unity 400 spectrometer. Proton NMR spectra were recorded as a function of increasing field gradient, using bipolar pulses and LEDS pulse sequence.

Amplitude of the glyphosate resonance was measured in each spectrum, and the natural logarithm of amplitude was plotted against the square of field gradient. An illustrative example of such a plot is shown in Figure 1, for composition 24-04. Two straight-line components, corresponding to a "free" pool and an "entrapped" pool of glyphosate, were clearly distinguishable in all compositions except 24-01, which had no measurable "entrapped" pool. In compositions having an "entrapped" pool, the diffusion coefficients of this pool were extremely low, of the order of 10^{-10} cm^2/s , indicating strong binding or entrapment of the glyphosate by supramolecular structures in these compositions. Except in composition 24-01, the "entrapped" pool comprised about 20% to about 80% of all glyphosate present.

The fraction of the glyphosate in the "entrapped" pool was found to be correlated with the weight ratio of lecithin to MON 0818. As illustrated in Figure 2, the higher the lecithin to MON 0818 ratio, the greater was the fraction of glyphosate in the "entrapped" pool.

Example 25

Solid water-soluble granule compositions were prepared containing glyphosate ammonium salt, glufosinate ammonium salt and excipient ingredients as shown in

Table 25a.

Compositions 25-01 to 25-06 were prepared by the procedure described in Example 16, with the addition to the wet mix of glufosinate ammonium salt in the desired amount.

5

Table 25a

Granule composition	Weight %			
	Glyphosate a.e.	Glufosinate a.e.	Plurafac A-38	amine surfactant A
25-01	66.1	2.0		21.0
25-02	66.1	2.0	10.5	10.5
25-03	66.1	2.0	5.3	15.7
25-04	65.0	3.0		21.0
25-05	65.0	3.0	10.5	10.5
25-06	65.0	3.0	5.3	15.7

- Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 17 days after planting ABUTH and ECHCF. Evaluation of early symptom development was done 3 days after application (DAA), and evaluation of herbicidal effectiveness was done 17 days after application.

Roundup® Ultra was diluted and applied as a comparative treatment. Results, averaged for all replicates of each treatment, are shown in Table 25b.

15

Table 25b

Concentrate composition	Glyphosate and glufosinate rates g a.e./ha	% Inhibition			
		ABUTH		ECHCF	
		3 DAA	17 DAA	3 DAA	17 DAA
Roundup® Ultra	100 + 0	0	34	0	37
	200 + 0	0	81	0	76
	400 + 0	0	97	0	93
	600 + 0	0	99	0	94
25-01	100 + 3	0	30	0	36
	200 + 6	0	76	0	75
	400 + 12	2	96	0	86
	600 + 18	14	98	6	93

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Concentrate composition	Glyphosate and glufosinate rates g a.e./ha	% Inhibition			
		ABUTH		ECHCF	
		3 DAA	17 DAA	3 DAA	17 DAA
25-02	100 + 3	0	71	0	44
	200 + 6	0	92	0	77
	400 + 12	10	95	1	88
	600 + 18	16	96	6	91
25-03	100 + 3	0	66	0	49
	200 + 6	0	89	0	81
	400 + 12	12	97	8	98
	600 + 18	17	99	14	93
25-04	100 + 4.5	0	32	0	35
	200 + 9	0	80	0	77
	400 + 18	12	92	4	83
	600 + 27	17	91	9	85
25-05	100 + 4.5	0	67	0	47
	200 + 9	5	86	0	75
	400 + 18	13	91	9	88
	600 + 27	20	94	17	92
25-06	100 + 4.5	0	70	0	53
	200 + 9	8	90	0	83
	400 + 18	14	91	11	85
	600 + 27	18	91	15	88

Compositions 25-02 and 25-03 of the invention gave superior herbicidal effectiveness to composition 25-01 which contained amine surfactant A but did not contain the alkylether surfactant Plurafac™ A-38. Likewise, compositions 25-05 and 25-06 of the invention gave superior herbicidal effectiveness to composition 25-04.

Example 26

Aqueous suspension concentrate compositions were prepared containing glyphosate isopropylammonium salt, oxyfluorfen and surfactants as shown in Table 26a. Surfactant J is the tallowamine-based surfactant used in formulating Roundup® Ultra.

Compositions 26-01 and 26-02 were prepared by the following procedure. A 10% by weight aqueous solution of Surfactant J was first prepared. To this solution in a wide-mouthed jar was added oxyfluorfen powder, technical grade (95%) in an amount calculated to provide a 41% by weight suspension of oxyfluorfen active ingredient (a.i.). The jar was then placed in an Eiger mill where the suspension was

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26X

milled for 2 hours at 3000 rpm in a cooling bath at 10°C. Particle size analysis of the resulting milled oxyfluorfen showed a volume mean diameter of 2.5 µm and a volume median diameter of 1.7 µm. The surfactant, in this case Surfactant J, was present to facilitate the milling operation.

- 5 Glyphosate isopropylammonium salt in the form of MON 0139 (46% by weight glyphosate a.e.) was mixed with the 41% milled oxyfluorfen prepared as above in a weight ratio of glyphosate a.e. to oxyfluorfen a.i. of 12:1. (As the milled oxyfluorfen contained approximately 6% by weight Surfactant J, a small amount of this surfactant was contributed along with oxyfluorfen to the final composition; the
- 10 amount is believed small enough to be negligible in affecting herbicidal effectiveness.) Also added were surfactants selected as shown in Table 26a, colloidal particulate silica (a blend of Aerosil™ 380 and Aerosil™ MOX-80 of Degussa), propylene glycol, sodium sulfite and water in the amounts listed below (percentages are by weight):

15	MON 0139 (46% glyphosate a.e.)	67.00%
	oxyfluorfen (41% milled)	6.30%
	Aerosil™ 380	1.45%
	Aerosil™ MOX-80	0.25%
	surfactant(s) and coupling agent	(see Table 26a)
20	sodium sulfite	0.20%
	water	to 100.00%

- The above ingredients were thoroughly agitated for about 5 minutes or until a homogeneous suspension was formed. Ethoquad™ T/20 of Akzo is a polyoxyethylene quaternary tallowalkylmethylammonium chloride surfactant having
- 25 an average of about 10 oxyethylene units per molecule. Plurafac™ A-38 of BASF is a polyoxyethylene C₁₆₋₁₈ alkylether having an average of about 27 oxyethylene units per molecule. Composition 26-01 was included for comparative purposes only.

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Table 26a

Concentrate composition	Weight %					
	Glyphosate a.e.	Oxyfluorfen a.i.	Plurafac A-38	Ethoquad T/20	Surfactant J ¹	Coupling agent
26-01	30.8	2.6			14.5	0.2 ²
26-02	30.8	2.6	3.0	7.0		1.0 ³

¹ excluding minor amount added to oxyfluorfen during milling² monoethanolamine³ propylene glycol

- 5 Filaree (*Erodium* sp., EROSS) and annual bluegrass (*Poa annua*, POAAN) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 36 days after planting EROSS and POAAN. Evaluation of early symptom development was done 4 days after application (DAA), and evaluation of herbicidal effectiveness was done 20 days after application.

- 10 Roundup® Ultra was diluted and applied as a comparative treatment, both alone and in tank-mixture with Goal® 2XL herbicide of Rohm & Haas, an emulsifiable concentrate formulation of oxyfluorfen. The tank-mixture was prepared to give a 12:1 weight ratio of glyphosate a.e. to oxyfluorfen a.i. Results, averaged for
- 15 all replicates of each treatment, are shown in Table 26b.

Table 26b

Concentrate composition	Glyphosate and oxyfluorfen rates g a.e., a.i./ha	% Inhibition			
		EROSS		POAAN	
		4 DAA	20 DAA	4 DAA	20 DAA
Roundup® Ultra	400 + 0	0	57	0	50
	600 + 0	0	72	0	63
	800 + 0	3	93	0	78
	1000 + 0	8	93	2	88
Roundup® Ultra + Goal® 2XL tank-mixture	400 + 33	10	33	12	63
	600 + 50	17	45	13	65
	800 + 67	20	65	17	68
	1000 + 83	20	72	18	75
26-01	400 + 33	8	22	5	48
	600 + 50	18	53	10	73
	800 + 67	22	82	10	75
	1000 + 83	30	92	10	75

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Concentrate composition	Glyphosate and oxyfluorfen rates g a.e., a.i./ha	% Inhibition			
		EROSS		POAAN	
		4 DAA	20 DAA	4 DAA	20 DAA
26-02	400 + 33	10	50	8	58
	600 + 50	15	60	8	68
	800 + 67	20	90	8	77
	1000 + 83	25	93	8	83

Significant antagonism to the herbicidal effectiveness of glyphosate, especially on EROSS, was seen in this test with addition of oxyfluorfen. Composition 26-02 of the invention gave greatly reduced antagonism by comparison with the tank-mixture and also showed less antagonism than composition 26-01.

Example 27

Solid water-dispersible granule compositions were prepared containing glyphosate ammonium salt, oxyfluorfen and surfactants as shown in Table 26a.

Compositions 27-01 and 27-02 were prepared by the following procedure. In a food mixer were blended dry ammonium glyphosate powder (MON 8750 of Monsanto), a small amount of water (about 5 g per 100 g of all other ingredients), surfactants and ammonium sulfate as shown in Table 27a, and 41% milled oxyfluorfen prepared as described in Example 26. The weight ratio of glyphosate a.e. to oxyfluorfen a.i. was 12:1. After thorough blending, the resulting wet mix was extruded and dried as described in Example 16.

Compositions 27-03 and 27-04 were prepared by a similar procedure except that oxyfluorfen (technical grade, 95%) was melted and added to the wet mix instead of 41% milled oxyfluorfen. The amount of water added was increased to 7-8 g per 100 g of all other ingredients.

Table 27a

Granule composition	Weight %				
	Glyphosate a.e.	Oxyfluorfen a.i.	Plurafac A-38	Ethoquad T/20	Ammonium sulfate
27-01	37.0	3.1	6.25	6.25	40.5
27-02	37.0	3.1	3.12	9.38	40.5
27-03	37.0	3.1	6.25	6.25	40.5
27-04	37.0	3.1	3.12	9.38	40.5

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Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of plant treatment compositions were made 18 days after planting ABUTH and ECHCF. Evaluation of early symptom development was done 2
5 days after application (DAA), and evaluation of herbicidal effectiveness was done 18 days after application.

Roundup® Ultra was diluted and applied as a comparative treatment, both alone and in tank-mixture with Goal® 2XL herbicide of Rohm & Haas, an emulsifiable concentrate formulation of oxyfluorfen. The tank-mixture was prepared
10 to give a 12:1 weight ratio of glyphosate a.e. to oxyfluorfen a.i. Also included in this test were compositions 26-01 (as a comparative treatment) and 26-02 of Example 26. Results, averaged for all replicates of each treatment, are shown in Table 27b.

Table 27b

Concentrate composition	Glyphosate and oxyfluorfen rates g a.e., a.i./ha	% Inhibition			
		ABUTH		ECHCF	
		2 DAA	18 DAA	2 DAA	18 DAA
Roundup® Ultra	100 + 0	0	53	0	37
	200 + 0	0	83	0	72
	400 + 0	0	96	0	78
	600 + 0	0	100	0	87
Roundup® Ultra + Goal® 2XL tank-mixture	100 + 8	12	17	8	10
	200 + 17	18	57	12	70
	400 + 33	27	72	18	77
	600 + 50	32	77	25	82
26-01	100 + 8	10	47	7	30
	200 + 17	15	70	10	73
	400 + 33	18	85	17	78
	600 + 50	20	87	18	87
26-02	100 + 8	8	70	7	70
	200 + 17	13	90	10	75
	400 + 33	15	98	13	82
	600 + 50	17	99	20	90
27-01	100 + 8	7	53	5	68
	200 + 17	12	78	7	75
	400 + 33	13	88	12	82
	600 + 50	18	90	17	94

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Concentrate composition	Glyphosate and oxyfluorfen rates g a.e., a.i./ha	% Inhibition			
		ABUTH		ECHCF	
		2 DAA	18 DAA	2 DAA	18 DAA
27-02	100 + 8	5	67	5	72
	200 + 17	8	83	12	75
	400 + 33	12	95	15	85
	600 + 50	15	96	15	90
27-03	100 + 8	10	45	3	65
	200 + 17	18	78	10	75
	400 + 33	22	85	15	80
	600 + 50	22	93	18	83
27-04	100 + 8	7	80	3	72
	200 + 17	10	90	10	75
	400 + 33	13	98	12	82
	600 + 50	15	99	17	89

Significant antagonism to the herbicidal effectiveness of glyphosate, especially on ABUTH, was seen in this test with addition of oxyfluorfen. Compositions 26-02 and 27-01 to 27-04 of the invention gave greatly reduced antagonism by comparison with the tank-mixture and also showed less antagonism than composition 26-01.

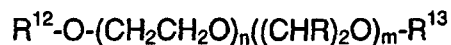
The preceding description of specific embodiments of the present invention is not intended to be a complete list of every possible embodiment of the invention. Persons skilled in this field will recognize that modifications can be made to the specific embodiments described here that remain within the scope of the present invention.

WHAT IS CLAIMED IS:

1. A method for eliciting biological activity of an anionic exogenous chemical substance applied to foliage of a plant, comprising

(i) preparing a plant treatment composition that comprises

- (a) water; having dissolved or dispersed therein
(b) an anionic exogenous chemical substance in a biologically effective amount;
(c) an alkylether surfactant component consisting of one or more surfactants each having the formula



wherein R^{12} is an aliphatic saturated or unsaturated hydrocarbyl group having about 16 to about 22 carbon atoms, n is an average number of about 5 to about 100, m is an average number of 0 to about 5, one R in each $-(CHR)_2O-$ group is hydrogen and the other R is methyl, and R^{13} is a hydrogen, C_{1-4} alkyl or C_{2-4} acyl group; and

- (d) an amine surfactant component consisting of one or more surfactants each having a molecular structure that comprises

- (1) a hydrophobic moiety having one or a plurality of independently saturated or unsaturated, branched or unbranched, aliphatic, alicyclic or aromatic C_{3-20} hydrocarbyl or hydrocarbylene groups joined together by 0 to about 7 ether linkages and having in total about 8 to about 24 carbon atoms, and
(2) a hydrophilic moiety comprising an amino group that is cationic or that can be protonated to become cationic, having attached directly thereto 1 to 3 oxyethylene groups or polyoxyethylene chains, these oxyethylene groups and polyoxyethylene chains comprising on average 1 to about 50 oxyethylene units per surfactant molecule, the hydrophobic moiety being attached either to the amino group or via an ether linkage to an oxyethylene unit;

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the weight ratio of the alkylether surfactant component to the amine surfactant component being about 1:10 to about 10:1; wherein the alkylether and amine surfactant components are present in total in an adjuvant amount of about 0.05 to about 0.5 parts by weight per part by weight of the anionic exogenous chemical substance, expressed as acid equivalent; and

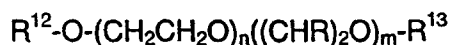
- (ii) applying a biologically effective amount of the plant treatment composition to foliage of the plant;

whereby the alkylether and amine surfactant components interact synergistically to elicit greater biological effectiveness of the anionic exogenous chemical substance than would be elicited by either component alone at the same total surfactant concentration in the plant treatment composition.

2. A method for eliciting biological activity of an anionic exogenous chemical substance applied to foliage of a plant, comprising

- (i) preparing a plant treatment composition that comprises

- (a) water; having dissolved or dispersed therein
(b) an anionic exogenous chemical substance in a biologically effective amount;
(c) an alkylether surfactant component consisting of one or more surfactants each having the formula



wherein R^{12} is an aliphatic saturated or unsaturated hydrocarbyl group having about 16 to about 22 carbon atoms, n is an average number of about 5 to about 100, m is an average number of 0 to about 5, one R in each $-(CHR)_2O-$ group is hydrogen and the other R is methyl, and R^{13} is a hydrogen, C_{1-4} alkyl or C_{2-4} acyl group; and

- (d) an amine surfactant component consisting of one or more surfactants each having a molecular structure that comprises

- (1) a hydrophobic moiety having one or a plurality of independently saturated or unsaturated, branched or unbranched, aliphatic, alicyclic or aromatic C_{3-20} hydrocarbyl or hydrocarbylene groups joined together by 0 to about 7 ether

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linkages and having in total about 8 to about 24 carbon atoms,
and

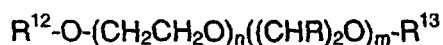
- (2) a hydrophilic moiety comprising an amino group that is cationic or that can be protonated to become cationic, having attached directly thereto 1 to 3 oxyethylene groups or polyoxyethylene chains, these oxyethylene groups and polyoxyethylene chains comprising on average 1 to about 50 oxyethylene units per surfactant molecule, the hydrophobic moiety being attached either to the amino group or via an ether linkage to an oxyethylene unit;

the weight ratio of the alkylether surfactant component to the amine surfactant component being about 1:10 to about 10:1; wherein the alkylether and amine surfactant components are present in total in an adjuvant amount of about 0.05 to about 0.5 parts by weight per part by weight of the anionic exogenous chemical substance, expressed as acid equivalent; and

- (ii) applying a biologically effective amount of the plant treatment composition to foliage of the plant within about 6 hours prior to rain or activation of overhead irrigation on the plant.

3. A method for eliciting herbicidal activity of an anionic herbicide applied to foliage of a plant, comprising

- (i) preparing a plant treatment composition that comprises
- (a) water; having dissolved or dispersed therein
 - (b) a first herbicide that is anionic and is present in a herbicidally effective amount;
 - (c) a second herbicide that is present in an amount effective to elicit a visible symptom of phytotoxicity in the plant within about 4 days after application to the foliage;
 - (d) an alkylether surfactant component consisting of one or more surfactants each having the formula



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wherein R^{12} is an aliphatic saturated or unsaturated hydrocarbyl group having about 16 to about 22 carbon atoms, n is an average number of about 5 to about 100, m is an average number of 0 to about 5, one R in each $-(CHR)_2O-$ group is hydrogen and the other R is methyl, and R^{13} is a hydrogen, C_{1-4} alkyl or C_{2-4} acyl group; and

(e) an amine surfactant component consisting of one or more surfactants each having a molecular structure that comprises

- (1) a hydrophobic moiety having one or a plurality of independently saturated or unsaturated, branched or unbranched, aliphatic, alicyclic or aromatic C_{3-20} hydrocarbyl or hydrocarbylene groups joined together by 0 to about 7 ether linkages and having in total about 8 to about 24 carbon atoms, and
- (2) a hydrophilic moiety comprising an amino group that is cationic or that can be protonated to become cationic, having attached directly thereto 1 to 3 oxyethylene groups or polyoxyethylene chains, these oxyethylene groups and polyoxyethylene chains comprising on average 1 to about 50 oxyethylene units per surfactant molecule, the hydrophobic moiety being attached either to the amino group or via an ether linkage to an oxyethylene unit;

the weight ratio of the alkylether surfactant component to the amine surfactant component being about 1:10 to about 10:1; wherein the alkylether and amine surfactant components are present in total in an adjuvant amount of about 0.05 to about 0.5 parts by weight per part by weight of the first herbicide, expressed as acid equivalent; and

(ii) applying a biologically effective amount of the plant treatment composition to foliage of the plant.

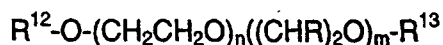
4. A plant treatment composition, comprising

- (a) water; having dissolved or dispersed therein
- (b) a first herbicide that is anionic and is present in a herbicidally effective amount;

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(c) a second herbicide that is present in an amount effective to elicit a visible symptom of phytotoxicity in the plant within about 4 days after application to the foliage;

(d) an alkylether surfactant component consisting of one or more surfactants each having the formula



wherein R^{12} is an aliphatic saturated or unsaturated hydrocarbyl group having about 16 to about 22 carbon atoms, n is an average number of about 5 to about 100, m is an average number of 0 to about 5, one R in each $-((CHR)_2O)-$ group is hydrogen and the other R is methyl, and R^{13} is a hydrogen, C_{1-4} alkyl or C_{2-4} acyl group; and

(e) an amine surfactant component consisting of one or more surfactants each having a molecular structure that comprises

(1) a hydrophobic moiety having one or a plurality of independently saturated or unsaturated, branched or unbranched, aliphatic, alicyclic or aromatic C_{3-20} hydrocarbyl or hydrocarbylene groups joined together by 0 to about 7 ether linkages and having in total about 8 to about 24 carbon atoms, and

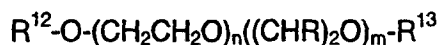
(2) a hydrophilic moiety comprising an amino group that is cationic or that can be protonated to become cationic, having attached directly thereto 1 to 3 oxyethylene groups or polyoxyethylene chains, these oxyethylene groups and polyoxyethylene chains comprising on average 1 to about 50 oxyethylene units per surfactant molecule, the hydrophobic moiety being attached either to the amino group or via an ether linkage to an oxyethylene unit;

the weight ratio of the alkylether surfactant component to the amine surfactant component being about 1:10 to about 10:1; wherein the alkylether and amine surfactant components are present in total in an adjuvant amount of about 0.05 to about 0.5 parts by weight per part by weight of the first herbicide, expressed as acid equivalent.

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ABSTRACT

A method of eliciting biological activity of an anionic exogenous chemical substance, for example the herbicide N-phosphonomethylglycine, is provided. This method comprises preparing a plant treatment composition having the anionic exogenous chemical substance dissolved or dispersed in water, together with (a) an alkylether surfactant component consisting of one or more surfactants each having the formula



wherein R^{12} is an aliphatic saturated or unsaturated hydrocarbyl group having about 16 to about 22 carbon atoms, n is an average number of about 5 to about 100, m is an average number of 0 to about 5, one R in each $-((CHR)_2O)-$ group is hydrogen and the other R is methyl, and R^{13} is a hydrogen, C_{1-4} alkyl or C_{2-4} acyl group; and (b) an amine surfactant component consisting of one or more surfactants each having a molecular structure that comprises (1) a hydrophobic moiety having one or a plurality of independently saturated or unsaturated, branched or unbranched, aliphatic, alicyclic or aromatic C_{3-20} hydrocarbyl or hydrocarbylene groups joined together by 0 to about 7 ether linkages and having in total about 8 to about 24 carbon atoms, and (2) a hydrophilic moiety comprising an amino group that is cationic or that can be protonated to become cationic, having attached directly thereto 1 to 3 oxyethylene groups or polyoxyethylene chains, these oxyethylene groups and polyoxyethylene chains comprising on average 1 to about 50 oxyethylene units per surfactant molecule, the hydrophobic moiety being attached either to the amino group or via an ether linkage to an oxyethylene unit. The weight ratio of the alkylether surfactant component to the amine surfactant component is about 1:10 to about 10:1; and the alkylether and amine surfactant components are present in total in an adjuvant amount of about 0.05 to about 0.5 parts by weight per part by weight of the anionic exogenous chemical substance, expressed as acid equivalent. The method further comprises applying the plant treatment composition to foliage of the plant.

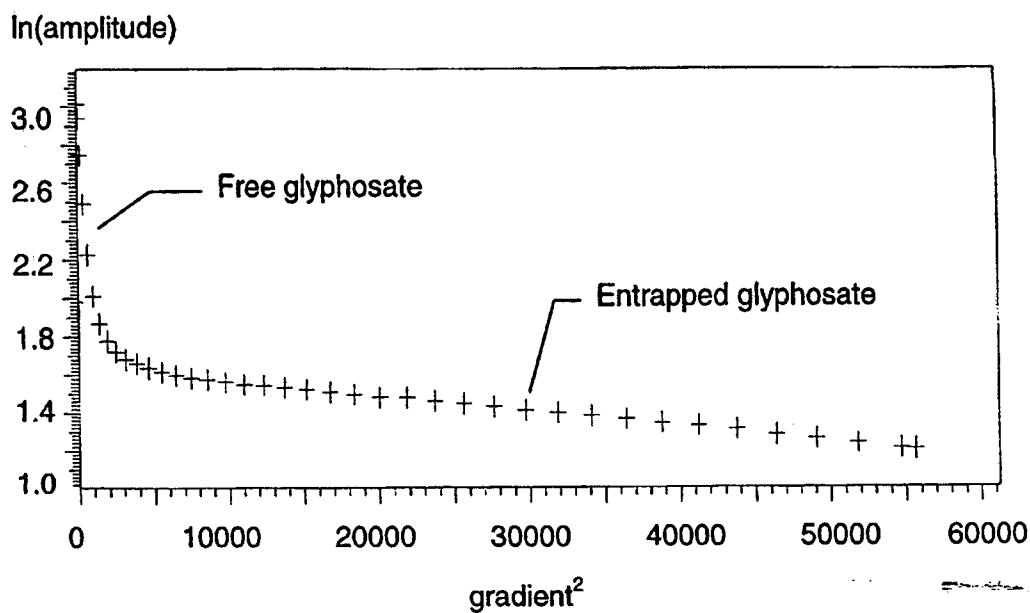
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Figure 1

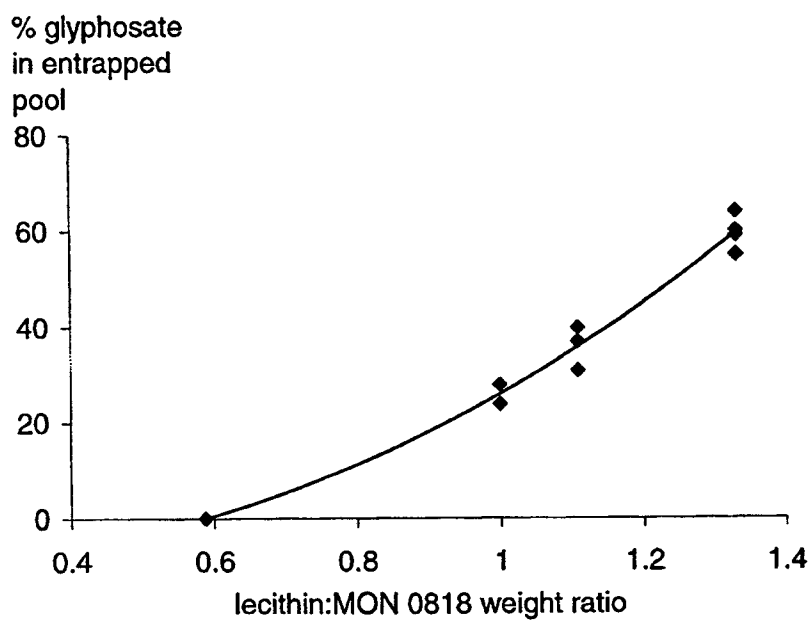
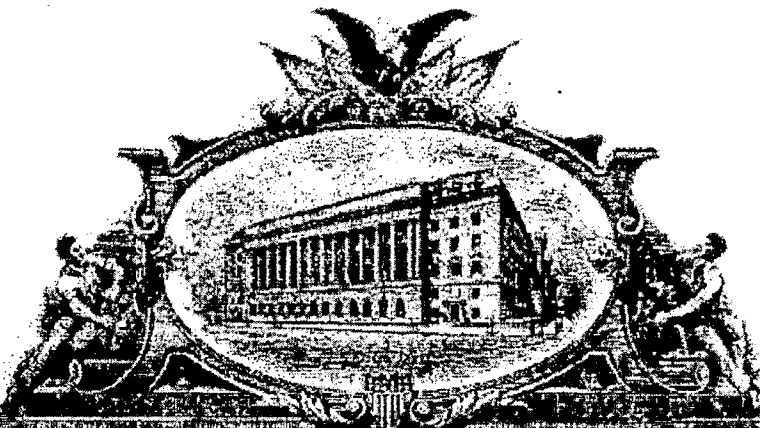


Figure 2



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LOS ESTADOS UNIDOS DE AMERICA

**A TODOS AQUELLOS A QUIENES LA PRESENTE CONCIERNE:
DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS**

Oficina de Patentes y Marcas de los Estados Unidos

11 de abril de 2000

LA PRESENTE ES PARA CERTIFICAR QUE LA ANEXA A ESTA ES UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA MAS ADELANTE QUE SATISFACEN LOS REQUISITOS PARA QUE SE OTORGUE UNA FECHA DE PRIORIDAD BAJO 35 USC 111..

SOLICITUD NUMERO: 60/130,756

FECHA DE PRESENTACION: 23 de abril de 1999



Por la Autoridad del
COMISIONADO DE PATENTES Y MARCAS

Firmado por
P. SWAIN

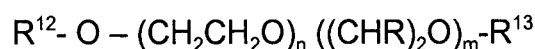
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REIVINDICACIONES

1. Un método para provocar la actividad biológica de una sustancia química exógena aniónica aplicada al follaje de una planta, que comprende

- (I) preparar una composición para el tratamiento de plantas que comprende
- (a) agua, que tiene disueltos o dispersos en ella
- (b) una sustancia química exógena aniónica en una cantidad efectiva para su aplicación biológica,
- (c) un componente de agente tensioactivo de alquiléter que consiste en uno o más agentes tensioactivos, cada uno con la fórmula



donde R^{12} es un grupo hidrocarbilo alifático saturado o no saturado que tiene alrededor de 16 a alrededor de 22 átomos de carbono, n es un número promedio de alrededor de 5 a alrededor de 100, m es un número promedio de 0 a alrededor de 5, un R en cada grupo $-(CHR)_2O-$ es hidrógeno y el otro R es metilo, y R^{13} es hidrógeno o un grupo C_{1-4} alquilo o C_{2-4} acilo, y

- (d) un componente de agente tensioactivo de amina que consiste en uno a más agentes tensioactivos, cada uno con una estructura molecular que comprende
- (1) una porción hidrofóbica que tiene un o una pluralidad de grupos C_{3-20} hidrocarbilo o hidrocarbilenos independientemente saturados o no saturados, ramificados o no ramificados, alifáticos, alicíclicos o aromáticos, unidos entre sí por 0 a alrededor de 7 uniones éter y con un total de alrededor de 8 a alrededor de 24 átomos de carbono, y
- (2) una porción hidrofílica que comprende un grupo amino que es catiónico, o que puede protonarse para que se torne catiónico, que tiene unido directamente a sí de 1 a 3 grupos de oxietileno o cadenas de polioxietileno, comprendiendo estos grupos de oxietileno o estas cadenas de polioxietileno un promedio de 1 a alrededor de 50 unidades de oxietileno por molécula de agente tensioactivo, estando la porción hidrofóbica unida directamente al grupo amino o, por medio de una unión éter, a una unidad de oxietileno;

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siendo la relación de peso del componente de agente tensioactivo de alquiléter al componente de agente tensioactivo de amina de alrededor de 1 a 10 a alrededor de 10 a 1, donde los componentes de agente tensioactivo de alquiléter y de amina están presentes en total en una cantidad coadyuvante de alrededor de 0,05 a alrededor de 0,5 partes por peso por parte por peso de la sustancia química exógena, expresada como equivalente ácido; y

- (II) aplicar una cantidad biológicamente efectiva de la composición para el tratamiento de plantas al follaje de la planta;

en donde los componentes de agente tensioactivo de alquiléter y de amina interactúan sinérgicamente para provocar una mayor efectividad biológica de la sustancia química exógena que la provocada por cada componente solo a la misma concentración total de agente tensioactivo en la composición de tratamiento de la planta.

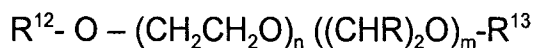
2. Un método para provocar la actividad biológica de una sustancia química exógena aniónica aplicada al follaje de una planta, que comprende

- (I) preparar una composición para el tratamiento de plantas que comprende

(a) agua, que tiene disueltos o dispersos en ella

(b) una sustancia química exógena aniónica en una cantidad efectiva para su aplicación biológica,

(c) un componente de agente tensioactivo de alquiléter que consiste en uno o más agentes tensioactivos, cada uno con la fórmula



donde R^{12} es un grupo hidrocarbilo alifático saturado o no saturado que tiene alrededor de 16 a alrededor de 22 átomos de carbono, n es un número promedio de alrededor de 5 a alrededor de 100, m es un número promedio de 0 a alrededor de 5, un R en cada grupo $-(CHR)_2O-$ es hidrógeno y el otro R es metilo, y R^{13} es hidrógeno o un grupo C_{1-4} alquilo o C_{2-4} acilo, y

(d) un componente de agente tensioactivo de amina que consiste en uno a más agentes tensioactivos, cada uno con una estructura molecular que comprende

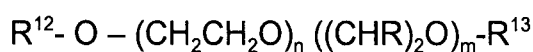
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- (1) una porción hidrofóbica que tiene un o una pluralidad de grupos C_{3-20} hidrocarbilo o hidrocarbilenos independientemente saturados o no saturados, ramificados o no ramificados, alifáticos, alicíclicos o aromáticos, unidos entre sí por 0 a alrededor de 7 uniones éter y con un total de alrededor de 8 a alrededor de 24 átomos de carbono, y
 - (2) una porción hidrofílica que comprende un grupo amino que es catiónico, o que puede protonarse para que se torne catiónico, que tiene unido directamente a sí de 1 a 3 grupos de oxietileno o cadenas de polioxietileno, comprendiendo estos grupos de oxietileno o estas cadenas de polioxietileno un promedio de 1 a alrededor de 50 unidades de oxietileno por molécula de agente tensioactivo, estando la porción hidrofóbica unida directamente al grupo amino o, por medio de una unión éter, a una unidad de oxietileno;
- siendo la relación de peso del componente de agente tensioactivo de alquiléter al componente de agente tensioactivo de amina de alrededor de 1 a 10 a alrededor de 10 a 1, donde los componentes de agente tensioactivo de alquiléter y de amina están presentes en total en una cantidad coadyuvante de alrededor de 0,05 a alrededor de 0,5 partes por peso por parte por peso de la sustancia química exógena, expresada como equivalente ácido, y
- (II) aplicar una cantidad biológicamente efectiva de la composición para el tratamiento de plantas al follaje de la planta dentro de las 6 horas anteriores a la lluvia o a la activación de la irrigación sobre la planta.
3. Un método para provocar la actividad biológica de una sustancia química exógena aniónica aplicada al follaje de una planta, que comprende
 - (I) preparar una composición de tratamiento de plantas que comprende
 - (a) agua, que tiene disueltos o dispersos en ella
 - (b) un primer herbicida que es aniónico en una cantidad efectiva para su aplicación biológica,
 - (c) un segundo herbicida en una cantidad efectiva para provocar un síntoma visible de fitotoxicidad en una planta dentro de los siguientes 4 días a la aplicación al

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follaje de la planta;

- (d) un componente de agente tensioactivo de alquiléter que consiste en uno o más agentes tensioactivos, cada uno con la fórmula



donde R^{12} es un grupo hidrocarbilo alifático saturado o no saturado que tiene alrededor de 16 a alrededor de 22 átomos de carbono, n es un número promedio de alrededor de 5 a alrededor de 100, m es un número promedio de 0 a alrededor de 5, un R en cada grupo $-(CHR)_2O-$ es hidrógeno y el otro R es metilo, y R^{13} es hidrógeno o un grupo C_{1-4} alquilo o C_{2-4} acilo, y

- (e) un componente de agente tensioactivo de amina que consiste en uno a más agentes tensioactivos, cada uno con una estructura molecular que comprende

(1) una porción hidrofóbica que tiene un o una pluralidad de grupos C_{3-20} hidrocarbilo o hidrocarbilo independientemente saturados o no saturados, ramificados o no ramificados, alifáticos, alicíclicos o aromáticos, unidos entre sí por 0 a alrededor de 7 uniones éter y con un total de alrededor de 8 a alrededor de 24 átomos de carbono, y

(2) una porción hidrofílica que comprende un grupo amino que es catiónico, o que puede protonarse para que se torne catiónico, que tiene unido directamente a sí de 1 a 3 grupos de oxietileno o cadenas de polioxietileno, comprendiendo estos grupos de oxietileno o estas cadenas de polioxietileno un promedio de 1 a alrededor de 50 unidades de oxietileno por molécula de agente tensioactivo, estando la porción hidrofóbica unida directamente al grupo amino o, por medio de una unión éter, a una unidad de oxietileno;

siendo la relación de peso del componente de agente tensioactivo de alquiléter al componente de agente tensioactivo de amina de alrededor de 1 a 10 a alrededor de 10 a 1, donde los componentes de agente tensioactivo de alquiléter y de amina están presentes en total en una cantidad coadyuvante de alrededor de 0,05 a alrededor de 0,5 partes por peso por parte por peso del primer herbicida, expresada como equivalente ácido; y

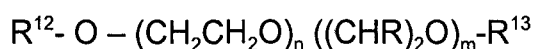
(II) aplicar una cantidad biológicamente efectiva de la composición de tratamiento

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de plantas al follaje de la planta.

4. Una composición para tratamiento de plantas, que comprende

- (a) agua, que tiene disueltos o dispersos en ella
- (b) un primer herbicida que es aniónico en una cantidad efectiva para su aplicación biológica,
- (c) un segundo herbicida en una cantidad efectiva para provocar un síntoma visible de fitotoxicidad en una planta dentro de los siguientes 4 días a la aplicación al follaje de la planta;
- (d) un componente de agente tensioactivo de alquiléter que consiste en uno o más agentes tensioactivos, cada uno con la fórmula



donde R^{12} es un grupo hidrocarbilo alifático saturado o no saturado que tiene alrededor de 16 a alrededor de 22 átomos de carbono, n es un número promedio de alrededor de 5 a alrededor de 100, m es un número promedio de 0 a alrededor de 5, un R en cada grupo $-(CHR)_2O-$ es hidrógeno y el otro R es metilo, y R^{13} es hidrógeno o un grupo C_{1-4} alquilo o C_{2-4} acilo, y

- (e) un componente de agente tensioactivo de amina que consiste en uno a más agentes tensioactivos, cada uno con una estructura molecular que comprende
 - (1) una porción hidrofóbica que tiene un o una pluralidad de grupos C_{3-20} hidrocarbilo o hidrocarbilenos independientemente saturados o no saturados, ramificados o no ramificados, alifáticos, alicíclicos o aromáticos, unidos entre sí por 0 a alrededor de 7 uniones éter y con un total de alrededor de 8 a alrededor de 24 átomos de carbono, y
 - (2) una porción hidrofílica que comprende un grupo amino que es catiónico, o que puede protonarse para que se torne catiónico, que tiene unido directamente a sí de 1 a 3 grupos de oxietileno o cadenas de polioxietileno, comprendiendo estos grupos de oxietileno o estas cadenas de polioxietileno un promedio de 1 a alrededor de 50 unidades de oxietileno por molécula de agente tensioactivo, estando la porción hidrofóbica unida directamente al grupo amino o, por medio de una unión éter, a una unidad de oxietileno;

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siendo la relación de peso del componente de agente tensioactivo de alquiléter al componente de agente tensioactivo de amina de alrededor de 1 a 10 a alrededor de 10 a 1, donde los componentes de agente tensioactivo de alquiléter y de amina están presentes en total en una cantidad coadyuvante de alrededor de 0,05 a alrededor de 0,5 partes por peso por parte por peso del primer herbicida, expresada como equivalente ácido.