



DELEGATURA PROPIEDAD INDUSTRIAL

División de Nuevas Creaciones

PCT
SOLICITUD

PATENTE DE INVENCION

ENTRADA EN FASE NACIONAL

07-39593

21. **EXPEDIENTE No.**

54. **TITULO**

AGENTES TENSIOACTIVOS DE ALOUILAMINA CUATERNARIA ALCOXILADA

PARA GLIFOSATO

51. **CLASIFICACION INTERNACIONAL**

71. **SOLICITANTE**

MONSANTO TECHNOLOGY LLC.

DOMICILIO

SAINT LOUIS, MO 63167, ESTADOS UNIDOS DE AMERICA

74. **APODERADO**

JUAN PABLO CADENA SARMIENTO

22. **SANTAFE DE BOGOTA, D.C.**

F.N. 13-04-2007

Cesión, Aclarar Solicitante

AS: 103.515



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-039583-00000-0000

Fecha: 2007-04-20 15:58:46 Dep. 2020 NUECREACIONE
Tm. 11 PATENTEIYII Evs: 379 FASENACIONALII
Act. 411 PRESENTACION Folios: 188

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

1

SOLICITUD DE:



Patente de Invención.



Patente de Modelo de Utilidad.



Capítulo I.



Capítulo II.

2

SOLICITANTE
(71)

Nombre: MONSANTO TECHNOLOGY LLC.

Dirección: 800 North Lindberg Blvd., Saint Louis,
MO 63167, Estados Unidos de América
Nacionalidad o Domicilio: Estados Unidos
Lugar de Constitución: Estados Unidos
Teléfono: Fax:
E-mail

IDENTIFICACION

C.C. ☐ NIT ☐C.E. ☐ Otro ☐

Cual _____

Número _____

3

REPRESENTANTE
O APODERADO

Nombre: JUAN PABLO CADENA SARMIENTO

Dirección: Cra. 7 No. 71-21 Torre B – Piso 4

Teléfono: 744-2200 Fax: 742-2200

E-mail:

IDENTIFICACION

C.C. ☒ NIT ☐C.E. ☐ Otro ☐

Cual _____

Número 80.410.337 TP 57492

4

INVENTOR (ES)
(72)

Nombre: Shawn Zhu, William Abraham, John Hemming-Haus

Dirección: 132 Devon Farms Road, Stormville, NY 12582 (US); 17153 Lafayette Trails Drive, Wilwood,
MO 63038 (US); Monsanto Company, 800 N. Lindbergh Boulevard, St. Louis, MO 63167, Estados
Unidos de América (Respectivamente)

Nacionalidad o Domicilio: Estados Unidos de América (Respectivamente)

5 PCT (86)

Solicitud Internacional No. PCT/US2005/034076 Fecha 23-09-2005Publicación Internacional No. WO 2006/034426 A1 Fecha 30-03-2006Título (54): AGENTES TENSIOSACTIVOS DE ALQUILAMINA CUATERNARIA ALCOXILADA PARA GLIFOSATO

7 Clasificación Internacional (51) _____

8 Prioridad

SI ☒NO ☐

(33) País de Origen

US

(32) Fecha

23-09-2004

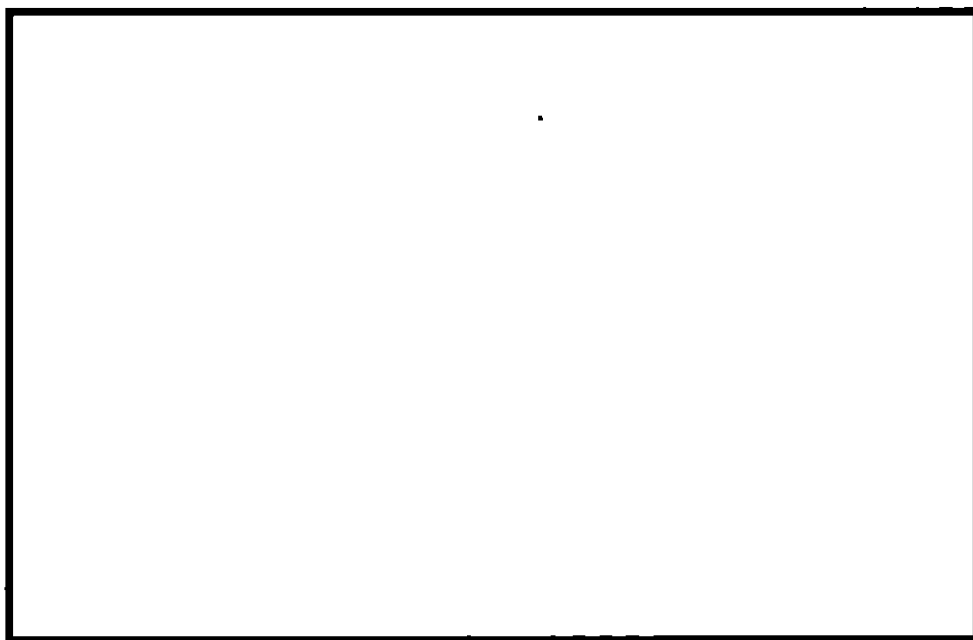
(31) Número de Solicitud

60/612,598

9 Comprobante de pago No. 07-23.441 Fecha 20-04-2007

Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página

- ☒ Comprobante de pago de la tasa de presentación de la solicitud. \$482.000
- ☒ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☒ Poderes, si fuere el caso. Fotocopia autenticada
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☐ Arte final 12x12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☒ Otros: Reivindicaciones Modificadas
Documentos PCT
Tarjeta de Propietarios

11 FIGURA CARACTERÍSTICA:**12** Solicito la concesión de la patente,NOMBRE: JUAN PABLO CADENA SARMIENTO

FIRMA:

C.C. 80.410.337 de Usaquén TP 57492 del C.S.J.

Instrucciones para la presentación de los anexos, ver reverso de esta página.

As 103.575
3

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-039593- -00000-0000

Fecha: 2007-04-20 15:58:48 Dep. 2020 NUECREACIONI
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALI
Act. 411 PRESENTACION Folios: 188

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 07 - 23,441
FECHA : MARZO 21 DE 2007

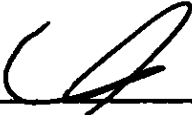
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	59310780	21/03/2007	16,746,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	482,000.00
		TOTAL :	\$ 482,000.00

SON: CUATROCIENTOS OCHENTA Y DOS MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES

PATENTE ☒ PCT/US2005/034076 MODELO DE UTILIDAD ☐ DISEÑO INDUSTRIAL ☐

SOLICITANTES/ S. RAZON SOCIAL O APELLIDOS Y NOMBRES MONSANTO TECHNOLOGY LLC.

DOMICILIO SAINT LOUIS, MO 63167, ESTADOS UNIDOS DE AMERICA

APODERADO JUAN PABLO CADENA SARMIENTO

TITULO AGENTES TENSIOACTIVOS DE ALOUILAMINA CUATERNARIA ALCOXILADA PARA GLIFOSATO

CLASIFICACION

EXPEDIENTE No. FECHA DE SOLICITUD BOLLO MICROFILM

CERTIFICADO No. FECHA DE CONCESION VIGENCIA DESDE HASTA

PRORROGA CAMBIO DE NOMBRE

TRASPASO A

INVENTOR (ES) SHAWN ZHU, WILLIAM ABRAHAM, JOHN HEMMING-HAUS

OTROS

OFICINA DE COMUNICACIONES

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 March 2006 (30.03.2006)

PCT

(18) International Publication Number
WO 2006/034426 A1

(51) International Patent Classification: A01N 57/20, 25/30, A01P 13/00 H (A01N 57/20, 25/30)

(21) International Application Number: PCT/US2005/034076

(22) International Filing Date: 23 September 2005 (23.09.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 60612,998 23 September 2004 (23.09.2004) US

(71) Applicant (for all designated States except US): AKZO NOBEL N.V. (NL/NL); Velperweg 76, 6824 BM Arnhem (NL).

(72) Inventor, and

(73) Inventor/Applicant (for US only): ZHU, Shawn (US/US); 132 Devon Farms Road, Sherrills, NY 12582 (US); ABRAHAM, William (IN/US); 17153 Lafayette Trails Drive, Whitewood, MO 63038 (US); HUEMMINGHAUSE, John (US/US); Monsanto Company, 800 N. Lindbergh Boulevard, St. Louis, MO 63167 (US).

(74) Agent: MANCINI, Ralph, J.; Akzo Nobel Inc., Intellectual Property Department, 7 Livingstone Avenue, Dobbs Ferry, NY 10522-3408 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, FR, GB, GR, GT, HK, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SI, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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

WO 2006/034426 A1

(54) Title: ALKOXYLATED ALKYLAMINE QUATERNARY SURFACTANTS FOR GLYPHOSATE

(57) Abstract: The present invention relates to stable glyphosate formulations with improved efficacy by a highly effective alkoxy-ated alkylamine quaternary surfactant at a very low used level. The alkoxyated alkylamine quaternary surfactant is compatible in all salts of glyphosate formulations (including potassium and ammonium) EVEN AT VERY HIGH CONCENTRATION (470 - 600 g a.e./l).

5
6

ALKOXYLATED ALKYLAMINE QUATERNARY SURFACTANTS FOR GLYPHOSATE

FIELD OF THE INVENTION

The present invention relates to glyphosate formulations comprising alkoxyated alkylamine quaternary surfactants having improved herbicidal activity.

BACKGROUND OF THE INVENTION

N-phosphonomethylglycine, otherwise known as glyphosate, is well known in the art as an effective post-emergent foliar applied herbicide. Glyphosate is an organic compound with three acidic groups, and in its acid form is relatively insoluble in water. Glyphosate is, therefore, normally formulated and applied as a water-soluble salt. Although monobasic, dibasic and tribasic salts of glyphosate can be made, it has generally been preferred to formulate and apply glyphosate, in the form of a monobasic salt, for example as a mono-isopropylamine, mono-potassium or mono-ammonium salt, or a dibasic salt such as the diammonium salt. Glyphosate herbicidal formulations are known which effectively comprise a mixture of mono-ammonium and di-ammonium salt, i.e., where the molar ratio of ammonium ion to glyphosate anion in the formulation is between 1 and 2.

When the terms "ammonium", "monoammonium" and "diammonium" are used herein to refer to salts of glyphosate, these terms apply strictly to inorganic ammonium, i.e., NH_4^+ , unless the context demands otherwise. Glyphosate rates and concentrations given herein, even where the glyphosate is present as a salt or salts, are expressed as acid equivalent (a.e.) unless the context demands otherwise.

For many applications, glyphosate salts require the presence of a suitable surfactant for best herbicidal performance. The surfactant can be provided either in the form of a concentrate, or it can be added by the end-user to the diluted spray solution. The choice of surfactant can be important since there are wide variations among surfactants in their ability to enhance the herbicidal efficacy of glyphosate for particular applications.

Use of a highly concentrated aqueous formulation of glyphosate in the form of a salt made with the inorganic base ammonia and potassium is advantageous. Ammonia and potassium are readily available, low in molecular weights, and relatively soluble in water. Additionally,

64

they are natural nutrients for the growth of plants and other organisms. The use of ammonium and potassium salts of glyphosate for preparing aqueous concentrate formulations of glyphosate suitable for killing and controlling weeds and other plants has, however, been somewhat limited due to difficulties arising from chemical and physical properties of the ammonium and potassium salts of glyphosate, lack of suitable surfactants for preparing high-loaded liquid concentrates of such salts, reduced weed control, and requirement for complex processes for preparing liquid ammonium and potassium glyphosate compositions.

Accordingly, it is desirable to develop an aqueous glyphosate formulation (i) having high glyphosate a.e. loading, (ii) containing a suitable herbicidal efficacy enhancing surfactant that can be used for all salts of glyphosate, and (iii) having a optimized concentration at very low loading level of that surfactant to provide herbicidal effectiveness greater than that of commercial standard glyphosate salt formulations.

It is, therefore, an objective of the present invention to provide a storage-stable, highly concentrated aqueous formulation containing glyphosate together one or more agriculturally acceptable surfactants that enhance the herbicidal effectiveness of applications of the formulation.

It is a further objective of the present invention to provide a storage-stable, highly concentrated aqueous formulation containing glyphosate and one or more surfactants and having a superior level of herbicidal effectiveness by comparison with current commercial standard glyphosate salt formulations.

There is a particular need in the art for stable aqueous liquid formulations comprising a quaternary ammonium salt surfactant such as, e.g., a dialkoxylated dialkylammonium halide, and in particular for formulations comprising ammonium glyphosate and a dialkoxylated dialkylammonium salt surfactant. Such formulations are known to the art, but have generally required a significant fraction of a nonionic surfactant to maintain stability of the formulation. Additionally, the quaternary ammonium salt in many such formulations comprise the di(hydroxyethyl)methyl cocoamine, which is a highly effective

SUMMARY OF THE INVENTION

The present invention relates to glyphosate formulations having improved stability and bioefficacy comprising as an adjuvant, at least one alkoxyated alkylamine quaternary surfactant.

78

The aforementioned adjuvant can be employed at low dosage rates and is stable in all of the various salts of glyphosate even at very high concentration.

DETAILED DESCRIPTION OF THE INVENTION

Glyphosate formulations generally require one or more adjuvants in order to boost its bio-efficacy. The amount of adjuvant employed is typically a glyphosate acid:adjuvant ratio of about 3:1 to 5:1 or lower in order to achieve significant boosting effect. The cost associated with the use of the adjuvants and other additives in glyphosate formulations can be significant. Therefore, there is an ever increasing need to find a more effective and economical adjuvant for glyphosate.

Glyphosate is an acid with a very limited solubility in water while salts of glyphosate have very high solubility in water. Therefore, glyphosate formulations usually employ salts of glyphosate. Many counterions have been used commercially in glyphosate products. They include isopropylamine, monoethanolamine, sodium, trimethylsulfonium, potassium, and ammonium. Accordingly, there are numerous salts of glyphosate, and many more surfactant choices used in the formulations. However, the use of too many surfactants in a glyphosate formulation plant can create logistical problems in part due to the fact that separate storage vessels are required for each surfactant. This can be costly, and thus there is a need to minimize the number of surfactants used in a glyphosate formulation plant.

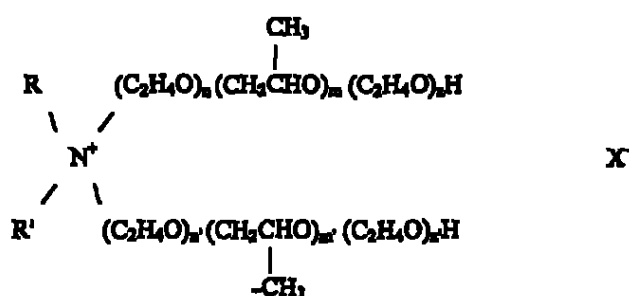
For liquid concentrate glyphosate formulations, practical glyphosate loading can be 360 g a.e./l or higher. It is known to skilled in the art that not many biologically useful surfactants can be incorporated in glyphosate formulations without phase separation at the practical loading of glyphosate and surfactants, in particular in the case of potassium and ammonium salts. One of the objectives is, therefore, to find a highly efficacious surfactant that can be used at very low levels in glyphosate formulations to improve the bioefficacy of glyphosate where the surfactant can be formulated into stable liquid concentrate formulations containing glyphosate as the potassium or ammonium salts at 470 - 600 g a.e./l.

The present invention meets this objective in providing glyphosate formulations having improved stability and bioefficacy comprising, as an adjuvant, at least one alkoxyated alkylamine quaternary surfactant. The aforementioned adjuvant can be employed at low dosage rates and is stable in all of the various salts of glyphosate even at very high glyphosate

89

concentration. In this regard it has been unexpectedly discovered that a class of surfactants exemplified by cocosamine quaternary surfactants with 2EO at a use level 3% (active quat) enhanced significantly the efficacy of glyphosate formulations in controlling unwanted weeds. It was found to be more effective than known commercial products and can be incorporated at very high loading of up to 600 g a.e./l potassium glyphosate and 470 g a.e./l ammonium glyphosate. At such high concentrations as 600 g a.e./l potassium glyphosate and 470 g a.e./l ammonium glyphosate, several of the surfactants used in current commercial glyphosate products will cause formulations to phase separate. Moreover, cocoamine-2EO quaternary surfactants are compatible with all of the various salts of glyphosate, even at very high loading.

The class of alkoxyated alkylamine quaternary surfactant adjuvants according to the present invention is represented by General Formula I, below:



wherein R is a straight or branched chain, saturated or unsaturated alkylene group having from 8 to 22 carbon atoms; R' is a straight or branched chain, saturated or unsaturated alkylene group having from 1 to 4 carbon atoms; and $n+n'$ is an integer of from 0-30, $m+m'$ is an integer of from 0 to 30, and $z+z'$ is an integer of from 0-30, with the proviso that $n+z$ is at least 1 and/or $n'+z'$ is at least 0 or 1, and X^- is a compatible anion such as methyl sulfate or Cl^- . In a preferred embodiment, the degree of ethoxylation is at least 1 and up to 30. Alternatively, the terminal ethoxy groups can be end-capped with, for example, a methyl or ethyl group.

A preferred cationic surfactant is methyl bis(2-hydroxyethyl)coco ammonium chloride. In certain preferred compositions of the invention the cationic surfactant is methyl bis(2-hydroxyethyl)cocoammonium chloride and there is no significant amount of secondary nonionic surfactant employed in the formulation. Nonionic surfactants such as polyoxyethylene alkylether including polyoxyethylene secondary alcohol having an average of about 3 to about 15 moles

9
10

ethylene oxide at a concentration greater than 5% with a cationics to nonionic ratio less than 5.2, are specifically excluded from the formulations of the present invention.

In another embodiment, the formulation of the invention contains less than about 0.5% by weight of other surfactants; in another embodiment less than about 0.2% by weight of other surfactants; in another embodiment less than about 0.1% other surfactants, and in still another embodiment no substantial amounts of other surfactants.

The water-soluble concentrate formulations of the present invention typically contain an amount of surfactant from about 0.5% to about 10% by weight in total of one or more surfactants. Preferably about 2% to about 8% by weight of surfactant is used although greater or lesser amounts may be employed if desired. The amounts and classes of surfactant used in compositions of the present invention are selected to provide high levels of herbicidal efficacy and a stable single-phase homogeneous mixture in the case of a liquid formulation. The invention is also applicable to solid formulations.

A composition of the invention can optionally comprise other additives such as ammonium sulfate, potassium sulfate, potassium chloride, sodium sulfate, urea, or mixtures thereof. A contemplated composition can optionally include a synergist, quick-burn additive, humectant, co-herbicide, dye, pigment, corrosion inhibitor, thickener, dispersing agent, calcium sequestrant, defoamer, antifreeze, pour-point depressant, or mixture thereof. Preferably, additives used in compositions of the present invention possess sufficient solubility or dispersibility in a concentrated aqueous glyphosate solution to allow desired concentrations to be attained.

Where a co-herbicide is included in the formulation, it is preferred that the co-herbicide be water-soluble. Examples of suitable co-herbicides are the salts of sulfonylurea, glufosinate, acifluorfen, asulam, benazolin, bentazon, bialaphos, bromacil, bromoxynil, chlorthalben, clopyralid, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, diquat, endothall, fenac, fenoxaprop, flazfop, flazifop, fluoroglyphosate, fomesafen, fosamine, haloxyfop, imazameth, imazamethabenz, imazamox, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, neptalam, nonanoic acid, paraquat, picloram, sulfamic acid, 2,3,6-TBA, TCA and triclopyr. A preferred co-herbicide is the IPA salt of 2,4-D. Alternatively, at least one herbicidally active compound employed can be selected from the group above, with or without the inclusion of glyphosate.

10
11

One or more process aids known to the skilled artisan can also be employed in the formulations of the present invention. Glycols are a preferred process aid. The preferred glycols include, but are not limited to propylene glycol, diethylene glycol, ethylene glycol, dipropylene glycol, mixtures thereof and the like. An example of a composition of the invention contains ammonium glyphosate in an amount of about 450 to about 500 g a.s./l, together with about 3% to about 5.2% by weight of methyl bis(2-hydroxyethyl) cocoammonium chloride, and about 0.75% to about 1.6% by weight of diethylene glycol. No nonionic surfactant is employed.

Formulations of the present invention may be generally prepared by mixing the glyphosate technical, together with other ingredients in a suitable mixing vessel with agitation, such as a blender. Heating may be needed to facilitate mixing.

This invention also relates to a herbicidal method of using a contemplated composition in an amount effective to kill or control unwanted vegetation by diluting the composition in water and applying the diluted composition to foliage of the vegetation to be killed or controlled.

Glyphosate formulations, as formulated in a composition of the invention, should be applied to plant foliage at an application rate sufficient to give the desired effect. Application rates are usually expressed as amount of glyphosate a.s. per unit area of land treated, e.g. grams a.s. per hectare (g a.s./ha). What constitutes a "desired effect" varies according to the standards and practice of those who investigate, develop, market and use glyphosate products. For example, the amount of glyphosate a.s. 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.

Preferred compositions of the invention provide enhanced herbicidal effectiveness by comparison with commercial standard formulations of glyphosate. "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 glyphosate formulation, such as a formulation of the present invention, is within the skill of the ordinary agricultural scientist. Those of skill in the art will likewise recognize that individual plant conditions, weather and growing conditions, as well as the specific formulation selected, will influence the degree of biological effectiveness achieved in practicing this invention. Useful

42

application rates can therefore depend upon all of the above conditions. Much information is known about appropriate application rates for glyphosate formulations in general. 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 glyphosate application rates that are herbicidally effective on particular species at particular growth stages in particular environmental conditions.

Various application methods may be employed including broadcast spraying, directed spraying or wiping the foliage with a diluted composition of this invention. Depending on the degree of control desired, the age and species of the plants, weather conditions and other factors, typically the glyphosate application rate is a herbicidally effective amount of about 0.1 to about 10 kg a.e./ha and preferably from about 0.25 to about 2.5 kg a.e./ha, although greater or lesser amounts may be applied.

Herbicidal compositions of glyphosate or derivatives thereof are used to control a very wide variety of plants worldwide. Glyphosate compositions of the invention can be applied to a plant in a herbicidally effective 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*, *Malva*, *Oryza*, *Ottobachloa*, *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 (*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 (*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 (*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*), ottobachloa (*Ottobachloa nodosa*), bahiagrass (*Paspalum notatum*), canarygrass (*Phalaris* spp.), 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.).

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*),alang (*Imperata cylindrica*), perennial ryegrass (*Lolium perenne*), guineagrass (*Panicum maximum*), dalliagrass (*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 (*Ulex europaeus*).

Thus, glyphosate compositions of the present invention, and a method for treating plants with such compositions, can be useful on any of the above species. In a particular contemplated method of use, a composition of the invention comprising glyphosate and surfactant is applied to foliage of crop plants 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.

Application of diluted compositions to foliage of plants is preferably accomplished by spraying, using any conventional means for spraying liquids, such as spray nozzles, atomizers, or the like. Compositions of the present invention can be used in precision farming techniques, in which apparatus is employed to vary the amount of glyphosate applied to different parts of a field, depending on variables such as the particular plant species present, soil composition, and the like. In one embodiment of such techniques, a global positioning system operated with the

spraying apparatus can be used to apply the desired amount of a diluted composition to different parts of a field.

A composition of the invention is preferably diluted to a sufficient degree in water to be readily sprayed using standard agricultural spray equipment. The rate per unit land area of diluted composition applied by spraying is conventionally known as "spray volume". Suitable spray volumes for the present invention vary depending upon a number of factors, including the plant species involved. Useful spray volumes for applying a diluted composition of the invention to foliage can range from about 25 to about 1,000 liters per hectare (l/ha), preferably about 50 to about 300 l/ha.

Particularly preferred formulations of the invention comprise stable aqueous liquid concentrates comprising an ammonium or diammonium salt of glyphosate and an alkoxyated quaternary alkylammonium salt surfactant. Formulations containing diammonium salts of glyphosate are particularly preferred. Generally, the molar ratio of ammonium ion to glyphosate ion in the formulation can range from about 0.8 to about 2.5. A ratio of ammonium ion to glyphosate ion of at least about 1.2 is preferred. Ammonium ion to glyphosate ion ratios between about 1.5 and about 2.2 may be particularly advantageous for some applications. Preferably, the formulation contains at least about 120 g/L, more preferably at least about 240 g/L, 300 g/L or 325 g/L, and still more preferably at least about 360 g/L glyphosate, a.e. In certain embodiments, the glyphosate a.e. content may be greater than about 400 g/L, greater than about 425 g/L or greater than about 450 g/L. The surfactant may correspond to the formula set forth above, or more generally to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^5$ and B is $(R^6O)_r(R^7O)_t(R^8O)_uR^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , and R^9 is independently selected from the group consisting of ethylene and isopropylene, each of R^5 and R^9 is independently selected from hydrogen, methyl and ethyl, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and $p + p' + q + q' + z + z'$ is at least about 2.

The weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is typically greater than 4.5:1, preferably greater than about 5.2:1, still more preferably greater than about 10:1 or 20:1. In certain especially preferred embodiments, the ammonium glyphosate concentrate is substantially devoid of any polyalkylene oxide alkyl ether surfactant, i.e., the concentration of the latter type of surfactant is below the level at which it has any functional effect as a surfactant and/or below the level at which it has any measurable effect on the cloud point of the formulation. It is also preferred that the weight ratio of the sum of all said alkoxyated alkyl quaternary alkylammonium salt surfactant(s) to the sum of all nonionic surfactants be greater than about 4.5:1, more preferably greater than about 5.2:1, and still more preferably greater than about 10:1 or 20:1. Advantageously, the ammonium glyphosate concentrate may be substantially devoid of any nonionic surfactant, "substantially devoid" being understood as described above.

For many applications, it is preferred that the sum of $(p + p' + q + q' + z + z') = 2$, i.e., that the surfactant is a 2EO dialkylammonium or other bis(hydroxyalkyl)dialkylammonium salt such as the bis(hydroxyethyl)methyl-cocoamine or bis(hydroxyethyl) methyltallowamina. For other applications, it may be preferred that $(p + p' + q + q' + z + z') \geq 3$. Where the quaternary alkylammonium salt is prepared by alkoxylation beyond the bis(hydroxyalkyl) species, the surfactant obtained is typically a mixture of homologs of varying extent of alkoxylation. Such surfactants can best be characterized by the number average value of $(p + p' + q + q' + z + z')$, sometimes referred to herein as W_0 . For example, alkoxyated quaternary alkylammonium surfactants for some applications may have a number average W_0 value between about 3 and about 7, or more particularly between about 4 and about 6. In other instances, an alkoxyated quaternary alkylammonium salt may have a W_0 value between about 6 and about 15, or more particularly between about 8 and about 12. Some formulations may comprise combinations of alkoxyated quaternary alkylammonium surfactants, e.g., a surfactant having a relatively low value of W_0 , for example about 2, or in the range of 3 to 7, and another surfactant having a relatively high value of W_0 , for example, in the range of about 8 to about 15 or between about 8 and about 12.

In certain preferred embodiments of the invention, the dialkoxyated quaternary alkylammonium salt surfactant comprises a mixture of homologs wherein R contains an average

FF
76

of between about 16 and about 18 carbon atoms. In certain particularly preferred embodiments, R is derived from tallow.

It has been found that stable aqueous liquid concentrates comprising diammonium glyphosate and dialkoxylated quaternary alkylammonium salt surfactants may be formulated at concentrations in excess of 38.0 wt.% glyphosate, a.e., and that such concentrates may exhibit a pH less than 7.3 and an ammonia concentration over the solution of less than about 750 ppm at 25°C.

In the ammonium glyphosate formulations of the invention, the weight ratios of glyphosate, a.e., to alkoxylated quaternary alkylammonium salt are typically between about 3 and about 20, more typically between about 3 and about 10. Particularly suitable diammonium glyphosate formulations may be prepared having a glyphosate to alkoxylated quaternary alkylammonium salt surfactant ratio between about 3.5 to about 9. Expressed on the basis of the total concentrate, the concentration of the sum of alkoxylated quaternary alkylammonium salt surfactant(s) may typically range from about 3 wt.% to about 12 wt.%, more typically from about 3.5 wt.% to about 10 wt.%.

The preferred ammonium glyphosate concentrates of the invention may also be formulated without substantial proportions of either ammonium sulfate or an alkylene glycol such as ethylene glycol or propylene glycol, or an alkylene ether glycol such as diethylene glycol.

For example, the ammonium sulfate content may be less than about 5 wt.%, less than about 3 wt.%, less than about 2 wt.% or less than about 1 wt.%. In fact, the concentrate may be substantially devoid of ammonium sulfate.

Similarly, the weight ratio of the sum of dialkoxylated quaternary alkylammonium salt surfactant to alkylene glycol and/or alkylene ether glycol may be greater than about 3.25, and is preferably greater than about 4, typically greater than about 5, and more typically greater than about 6, 8 or 10. The ratio of the sum of dialkoxylated quaternary alkylammonium salt surfactant to the sum of (all polyalkylene oxide alkyl ether surfactants + alkylene glycols + alkylene ether glycols) is greater than about 2, preferably greater than about 3, typically greater than about 5, 8 or 10.

Polyalkylene oxide alkyl ether surfactants have been used as to limit eye toxicity of glyphosate salt concentrates comprising alkoxylated quaternary alkylammonium salt surfactants,

while alkylene glycols and alkylene ether glycols are typically present in glyphosate concentrates that comprise alkoxyated quaternary alkylammonium salt and polyoxyethylene oxide alkyl ether surfactants. It has been discovered that the ammonium glyphosate concentrates of the present invention may be formulated with minimal concentrations of nonionic surfactants, minimal concentrations of alkylene ether glycols, minimal concentrations of alkylene glycols, or with minimal concentrations of either nonionic surfactants, alkylene glycols, or alkylene ether glycols. Certain preferred formulations may be substantially devoid of each, any, and/or all of these.

The absence or substantial absence of polyalkylene oxide alkyl ethers and other nonionics contributes to the stability of the formulations, because nonionic surfactants can compromise the stability of ammonium glyphosate concentrates comprising alkoxyated alkylammonium salt surfactants. In accordance with the invention, it has been discovered that diammonium glyphosate concentrates containing, e.g., 2EO, 5 EO and 10 EO methycocoquats and methyltallowquats can be formulated without either a nonionic surfactant, an alkylene glycol, or an alkylene ether glycol.

Further in accordance with the invention, it has been discovered that aqueous liquid ammonium glyphosate concentrates having surprisingly low eye toxicity can be formulated with minimal concentrations of polyalkylene oxide alkyl ethers or other nonionic surfactants. In fact, it has been found that such low eye toxicity formulations can be substantially devoid of nonionic surfactants. Prior to the present invention, it had been understood that, to meet the eye toxicity standards of at least some jurisdictions without incorporating a significant fraction of nonionic surfactant, the concentrations of cationic surfactants in ammonium glyphosate concentrates must be maintained at levels significantly lower than those desired for herbicidal efficacy. For example, it had been understood that, in an ammonium glyphosate concentrate having a loading greater than about 360 g/L glyphosate, a.e., the total concentration of dialkoxyated quaternary alkylammonium salt surfactant(s) should be maintained at not greater than about 3.5 wt.%, preferably not greater than about 3.2 wt.%, and/or that the weight ratio of such surfactant(s) to glyphosate, a.e., should be not greater than about 0.28, preferably not greater than about 0.25, typically not greater than about 0.20, 0.15, 0.13, 0.10 or 0.08. However, in accordance with the invention, it has been found that low eye toxicity can be preserved at significantly higher

surfactant concentration where certain novel principles are observed with regard to the formulation of the concentrate.

More particularly, it has been found that eye toxicity can be controlled by controlling the molar concentration of alkoxyated quaternary alkylammonium ion in the aqueous liquid concentrate, even at weight concentrations of alkoxyated quaternary alkylammonium salt sufficient to substantially enhance herbicidal efficacy. This may be achieved by selection of an alkoxyated quaternary alkylammonium salt surfactant having an average molecular alkylene oxide to amine ratio (W_0) in an intermediate range, thereby effectively diluting the molar concentration of quaternary ammonium ion as compared to a surfactant having a low value of W_0 in the range of, say, 2 to 4. Selection of a quaternary ammonium salt surfactant of such intermediate W_0 value thus achieves a relatively modest molar concentration of alkoxyated quaternary alkylammonium ion by what may be referred to as "intramolecular dilution." In various alternative embodiments, a high degree of herbicidal efficacy may be maintained at low levels of eye toxicity by "intermolecular dilution," i.e., by blending a relatively low molecular weight alkoxyated quaternary alkylammonium salt having a W_0 value in the range between about 2 and about 4 with a relatively high molecular weight alkoxyated quaternary alkylammonium salt having a W_0 value between about 7 and about 15.

Preferably, the R substituent in the formula set forth above comprises between about 8 and about 18 carbon atoms, more preferably between about 12 to about 18 carbon. Thus, an alkoxyated quaternary alkylammonium ion of intermediate W_0 value of about 5 to about 8 typically has a molecular weight between about 375 and about 650 preferably between about 400 and about 650. Expressed in another manner, a 5 to 8 EO ethoxyated quaternary alkylammonium chloride surfactant corresponding to the formula set forth above and derived from coconut or tallow has a "diluted" N content between about 0.0015 moles and about 0.0025 moles per gram surfactant. Such selection of relatively high molecular weight surfactants of intermediate W_0 values allows relatively high weight concentrations of alkoxyated quaternary alkylammonium surfactant to be incorporated into an aqueous ammonium glyphosate concentrate without exceeding the molar concentrations of the surfactant as described hereinabove. Without being held to a particular theory, it is also believed that the relatively high molecular weight alkyl and alkylene oxide substituents serve to reduce activity of the positively charged quaternary

18
19

ammonium ion at a given concentration thereof, which may permit a slightly higher surfactant loading to be used for better bioefficacy, without causing excessive eye irritation.

Based on the same preferred ranges of R substituents, a C₁₂ to C₁₈ alkoxyated quaternary alkylammonium salt having a low W₀ value between about 2 and about 4 typically has a molecular weight in the range between about 270 and about 450, and a C₁₂ to C₁₈ alkoxyated quaternary alkylammonium salt having a relatively high W₀ value between about 7 and about 15 has a molecular weight in the range between about 490 and about 925. Thus, for example, a blend having a weight ratio of a 2-4 EO methylcocoamine to 7-15 EO methylcocoamine or methyltallow amine between about 1:2 and 2:1 preferably comprises a diluted N content between about 0.0010 and about 0.0030, more preferably between about 0.0015 and about 0.0025, moles per gram surfactant.

Specific examples of blended alkoxyated quaternary alkylammonium salts include blends of an ethoxyated N-methylcocoammonium chloride sold under the trade designation "Ethaquad C12" having a W₀ value of 2 and a molecular weight of about 323 (quaternary 2 EO N-methylcocoammonium ion MW = 287; chloride ion MW = 35.5) and an ethoxyated N-methylcocoammonium chloride having a W₀ value of 10 and a molecular weight of 539 (quaternary 10 EO N-methylcocoammonium ion MW = 503; chloride ion MW = 35.5) or ethoxyated N-methyltallowammonium chloride having a W₀ value of 10 and a molecular weight of 759 (quaternary 10 EO N-methyltallowammonium ion MW = 723; chloride ion MW = 35.5).

Exemplary diammonium formulations that are substantially devoid of any nonionic surfactant are set out below:

Formulation A (360 g/L a.e.)

Diammonium glyphosate	30.3 wt.%, a.e.
N-methylcocoquat 2EO	7.90% a.i.

Formulation B (360 g/L a.e.)

Diammonium glyphosate	30.3 wt.%, a.e.
N-methyltallowquat 10 EO	2.60 wt.%, a.i.
Methylcocoquat 2EO	2.50 wt.% a.i.

19
20**Formulation C (360 g/L)**

Diammonium glyphosate	30.3 wt%, a.e.
N-methylcocoquat 5EO	5.1 wt%, a.i.

Formulation D (480 g/L)

Diammonium glyphosate	38.4 wt%, a.e.
N-methylcocoquat 2EO	7.2 wt%, a.i.

Formulation E (480 g/L)

Diammonium glyphosate	38.4 wt%, a.e.
N-methylcocoquat 2EO	4.62 wt%, a.i.

Formulation F (360 g/L a.e.)

Diammonium glyphosate	30.3 wt%, a.e.
N-methylcocoquat 2EO	2.00 wt%, a.i.
N-methylcocoquat 10EO	3.10 wt%, a.i.
Moles Quat N	0.123

Formulation G (360 g/L a.e.)

Diammonium glyphosate	30.3 wt%, a.e.
N-methylcocoquat 2EO	2.60 wt%, a.i.
N-methyltallowquat	2.50 wt%, a.i.
Moles Quat N	0.119

Formulation H (360 g/L a.e.)

Diammonium glyphosate	30.3 wt%, a.e.
N-methyltallowquat 5EO	5.10 wt%, a.i.
Tergitol nonionic surfactant	1.00 wt%, a.i.
C12, 14 Linear Alcohol (Tergitol)	9 mol EO

Formulation I (480 g/L a.e.)

20
21

Diammonium glyphosate	38.4 wt%, a.a.
N-methylcocoquat 2EO	4.65 wt%, a.i.
Nonionic surfactant	1.00 wt%, a.i.
OSP C18 Alcohol	9 mol EP 30 mol PO

All of these are brought to 100% with deionized water. The ammonium ion to glyphosate ion ratio is 1.9:1.

Of the formulations set forth above, Formulations B, C, F, G and H are of exceptionally low eye toxicity. These achieved a favorable rating of "yellow" according to the Acute Eye Irritation test per guideline OPPTS 870.2400 as issued by the United States Environmental Protection Agency, EPA 712-L-96-195, August 1998. These results contrast with the typical rating of "red" for high load ammonium glyphosate concentrates containing alkoxyated quaternary alkylammonium salts in the absence of relatively high concentrations of nonionic surfactants, or at least high nonionic to alkoxyated quaternary alkylammonium salt ratios.

The invention will now be illustrated by the following nonlimiting examples.

EXAMPLES

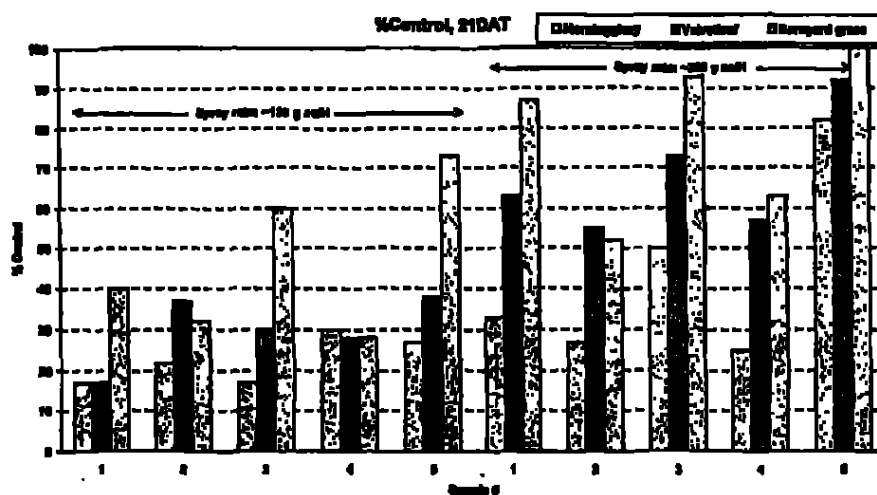
Three examples were performed by two different testing agents at three different times. Three replicas were used. The spray rate was in g a.e./H (grams of glyphosate acid per hectare). If the spray rate was the same, the glyphosate concentration was the same. All were sprayed with diluted solutions (from concentrates) and with the same spray volume. The percent control (% Control) was compared in all samples at 21 DAT (days after treatment).

Since it is the glyphosate anion that is biologically active, the concentration of a glyphosate formulation is typically expressed as grams of glyphosate acid per liter (g a.e./l) at 25C. Because of this, people compare glyphosate formulations generally at the same g a.e./l. The concentration of surfactant is typically expressed as grams of active surfactant per liter (g/l). Sometimes acid : surfactant ratio is also used. For example, if a formulation is 540 g a.e./l and surfactant is 90 g/l, the acid : surfactant ratio is 6. Therefore, the larger the acid:surfactant ratio, the less surfactant that is in the formulation.

EXAMPLE 1

Shown in the figure are five examples:

22



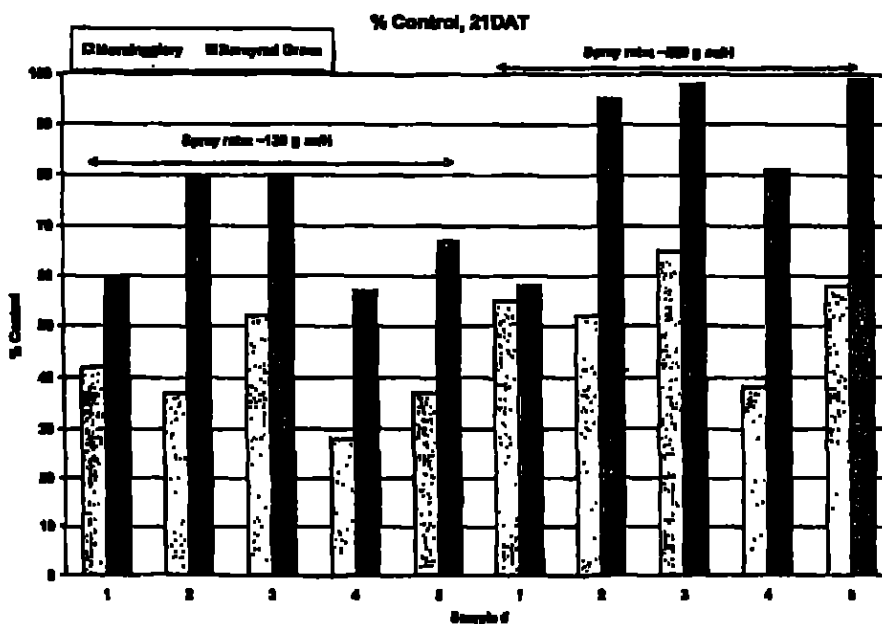
Sample #	Salt of glyphosate	Glyphosate Acid : Surfactant*	Surfactant used	Surfactant* Loading, wt%
1 (Roundup WeatherMax)	K	< 6	WeatherMax Surfactant	> 7
2 (potassium glyphosate)	K	N.A.	None	0
3 (Cationics + nonionics)	NH ₄	4.3	70% Cocoamine-2EO quat + 20% Diethylene glycol + 10% polyethylene (7) secondary C12-13 alkanol	8
4 (Cationics + nonionics)	NH ₄	9.4	70% Cocoamine-2EO quat + 20% Diethylene glycol + 10% polyethylene (7) secondary C12-13 alkanol	3.2
5 (Cationics)	NH ₄	10.1	75% Cocoamine-2EO quat + 25% Propylene glycol	3

*This ratio does not include glycol. The samples shown here are aqueous liquid formulations.

22
23

This example demonstrates that glyphosate without surfactant (Sample #2) did not provide the level of control as those with surfactants. In particular, Sample #5 had very low surfactant concentration, much lower than typical commercial products and lower than Sample #1, #3, and #4. However, Sample #5 still had higher % Control than all other samples. On the contrary, in order to achieve reasonable % Control, the surfactant system used in U.S. Patent No. 5998332, cationic and nonionics blend (Samples #3 and #4), needed to be used at about an acid:surfactant ratio of 4.3:1, a concentration more than twice as concentrated as that in Sample #5. At the same glyphosate concentration, the level of control provided by Sample #3 was less than for Sample #5 even though it had a surfactant concentration at twice the level found in Sample #5.

EXAMPLE 2



Shown in the figure are five samples. All were potassium glyphosate salt:

23
24

Sample #	Glyphosate Acid/ Surfactant* Ratio	Surfactant Used	Surfactant* Loading, wt%
1 (potassium glyphosate)	N.A.	None	0
2 (WeatherMax)	< 6	WeatherMax Surfactant	> 7
3 (Cationics)	7.51	75% Cocoamine-2EO quat + 25% propylene glycol	4
4 (Amine ethoxylate)	6.12	Tallowamine-10EO	6.5
5 (Etheramine ethoxylate)	4.4	Polyoxyethylene (5) C ₁₂ -C ₁₄ linear alcohol (oxypropyl) ₂ amine	9

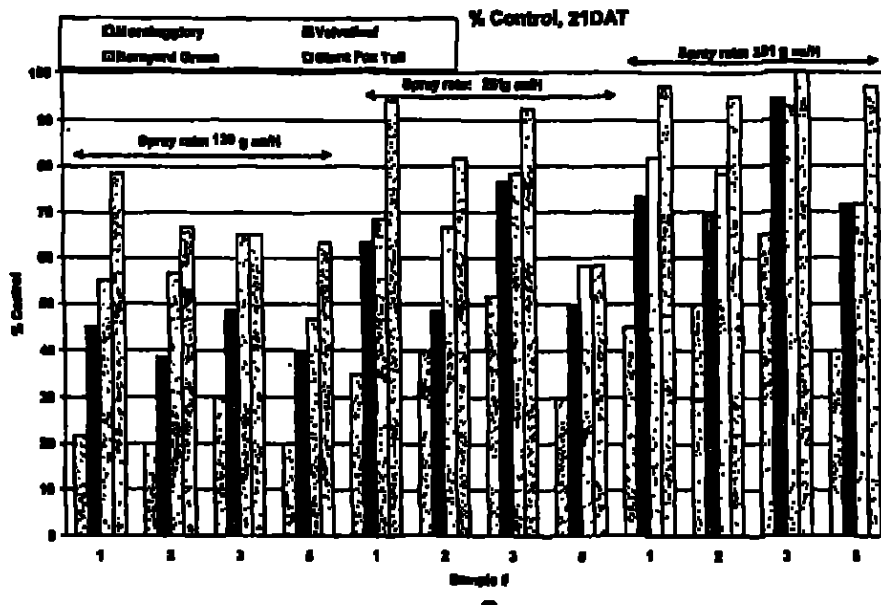
*This ratio does not include glycol. The samples shown here are aqueous liquid formulations.

In this example, Sample #3 had very low surfactant concentration, much lower than typical commercial products and lower than Samples #2, #4 and #5. However, Sample #3 still had higher or equivalent % Control than all other samples. At the same glyphosate concentration, Sample #3 had equivalent control to Sample #5 in % Control even though it had a surfactant concentration twice less concentrated than Sample #5.

Moreover, only Sample #3 was stable between -20 and 60C at a concentration of more than 540 g a.e./L.

207
25

EXAMPLE 3



Samples shown in the figure were the same as those in Example 2 (Sample #4 is not used here). Again, in this example, Sample #3 was equivalent to or better than the other samples in % Control.

As is shown in the above examples, it has been unexpectedly discovered that a highly effective and efficient surfactant, alkoxyated alkylamine quaternary, can improve significantly the efficacy of a glyphosate formulation. Moreover, the alkoxyated alkylamine quaternary surfactant is stable in all salts of glyphosate formulations (including potassium and ammonium) even at very high concentration (470 – 600 g a.e./l). This result is expected to provide significant cost savings in raw material for glyphosate formulations and will improve the logistics of handling surfactants in the plant.

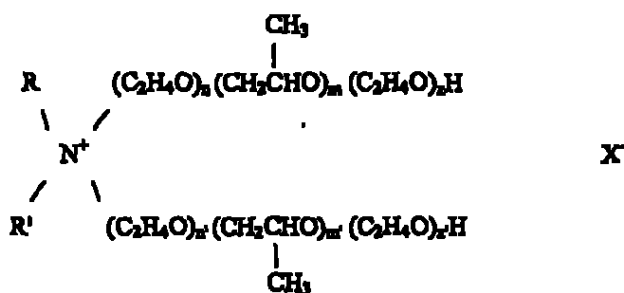
25
26

What is claimed is:

1. A stable, herbicidal formulation that comprises at least one herbicidally active compound and a surfactant adjuvant, wherein said surfactant adjuvant comprises at least one alkoxyated quaternary ammonium cationic surfactant.
2. The formulation of claim 1 wherein said formulation contains substantially no polyoxyethylene alkyl ethers.
3. The formulation of claim 2 wherein said formulation contains less than about 0.2% by weight of other surfactants.
4. The formulation of claim 3 wherein said formulation contains less than about 0.1% by weight of other surfactants.
5. The formulation of claim 4 wherein said formulation contains no substantial amounts of other surfactants.
6. The formulation of claim 1 wherein said herbicidally active compound is a glyphosate salt.
7. The formulation of claim 1 wherein said formulation is stable between -20 and 60°C, preferably -10 to 50°C and more preferably 0 and 40°C.
8. The formulation of claim 1 which additionally comprises at least one process aid.
9. The formulation of claim 8 wherein said process aid is a glycol.
10. The formulation of claim 1 wherein said alkoxyated quaternary compound is methyl bis(2-hydroxyethyl)coco ammonium chloride.

26
27

11. The formulation of claim 6 wherein the glyphosate salt is selected from the group sodium, potassium, ammonium, isopropylamine, monoethanolamine, diethanolamine, triethanolamine, trimethylsulfonium, and mixtures thereof.
12. The formulation of claim 11 wherein the glyphosate formulation is a stable liquid formulation with a concentration of glyphosate in the range of 360 – 600 g a.e./l, preferably 450 – 580 g a.e./l.
13. The formulation of claim 6 wherein the ratio of glyphosate (wt% a.e.) to the alkoxyated quaternary ammonium compound is between 4:1 and 100:1.
14. The formulation of claim 13 wherein the ratio of glyphosate (wt% a.e.) to the alkoxyated quaternary ammonium compound is between 7:1 to 40:1.
15. The formulation of claim 14 wherein the ratio of glyphosate (wt% a.e.) to the alkoxyated quaternary ammonium compound is between 10:1 to 30:1.
16. The formulation of claim 1 which additionally comprises a co-herbicide.
17. The formulation of claim 16 wherein said co-herbicide is selected from the group consisting essentially of sulfonylurea, acifluorfen, asulam, benazolin, bentazon, bialaphos, bromacil, bromoxynil, chlormamben, clopyralid, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, diquat, endosulf, fensu, fenoxsprop, flumprop, fluazifop, fluoroglycofen, florasafen, fosamine, glufosinate, haloxyfop, imazameth, imazamethabenz, imazamox, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naptalam, nonanoic acid, paraquat, picloram, sulfamic acid, 2,3,6-TBA, TCA, triclopyr, salts thereof, and mixtures thereof.
18. The formulation of claim 1 wherein said alkoxyated quaternary ammonium compound is of General Formula I, below:
-

27
28

wherein R is a straight or branched chain, saturated or unsaturated alkylene group having from 8 to 22 carbon atoms; R' is a straight or branched chain, saturated or unsaturated alkylene group having from 1 to 4 carbon atoms; and $n+n'$ is an integer of from 0-30, $m+m'$ is an integer of from 0 to 30, and $x+x'$ is an integer of from 0-30, with the proviso that $n+x$ is at least 1 and/or $n'+x'$ is at least 0 or 1, and X⁻ is an agriculturally compatible anion.

19. The formulation of claim 18 wherein said alkoxyated quaternary ammonium compound is methyl bis(2-hydroxyethyl)coco ammonium chloride.

20. The formulation of claim 19 wherein said formulation is a solid.

21. The formulation of claim 20 wherein said formulation comprises at least one alkoxyated quaternary surfactant and a glyphosate salt, wherein the surfactant:salt ratio is between 4:1 to 100:1.

22. The formulation of claim 1 wherein said at least one herbicidally active compound is selected from the group consisting essentially of sulfonylureas, acifluorfen, asulam, benazolin, bentazon, bialaphos, bromacil, bromoxynil, chloramben, clopyralid, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, diquat, endothall, fenac, fenoxaprop, flumprop, fluazifop, fluoroglyphofen, fomesafen, fosamine, glufosinate, haloxyfop, imazameth, imazamethabenz, imazamox, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naptalam, nonanoic acid, paraquat, picloram, sulfamic acid, 2,3,6-TBA, TCA, triclopyr, salts thereof, and mixtures thereof.

28
29

23. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 240 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.8 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^6$ and B is $(R^5O)_p(R^6O)_q(R^7O)_zR^9$ where each of R^2, R^3, R^4, R^5, R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, each of R^8 and R^9 is selected from the group consisting of hydrogen, methyl and ethyl, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $p + p' + q + q' + z + z'$ is at least about 2,

the weight ratio of the sum of all said alkoxyated alkyl quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) being greater than 4.5:1.

24. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) being greater than 4.5:1.

25. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) being greater than 5.2:1.

26. A stable aqueous liquid herbicidal concentrate as set forth in claim 25 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) being greater than 5.2:1.

27. A stable aqueous liquid herbicidal concentrate as set forth in claim 25 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) being greater than 10:1.

28. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) being greater than 10:1.

29. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 comprising at least about 325 g/l glyphosate, a.e.

30. A stable aqueous liquid herbicidal concentrate as set forth in claim 29 comprising at least about 360 g/L glyphosate, a.e.

31. A stable aqueous liquid herbicidal concentrate as set forth in claim 30 comprising at least about 400 g/L glyphosate, a.e.

32. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 containing not more than about 5 wt.% ammonium sulfate.

33. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 3.25.

34. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 4.

35. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein $(p + q + p' + q' + z + z') \geq 3$.

30
37

36. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein said alkoxyated quaternary alkylamine surfactant(s) have a W_0 value between about 3 and about 20, where W_0 is the average value of $(p + p' + q + q' + z + z')$ for said surfactant(s).

37. A stable aqueous liquid herbicidal concentrate as set forth in claim 36 wherein the value of W_0 is between about 3 and about 7.

38. A stable aqueous liquid herbicidal concentrate as set forth in claim 36 wherein the value of W_0 is between about 6 and about 15.

39. A stable aqueous liquid herbicidal concentrate as set forth in claim 36 comprising a plurality of alkoxyated quaternary alkylammonium surfactants, the value of W_0 for at least one of said plurality of surfactants being about 2, and the value of W_0 for the other of said surfactants being in the range of between about 8 and about 15.

40. A stable aqueous liquid herbicidal concentrate as set forth in claim 39 wherein R of at least one of said plurality of alkoxyated quaternary alkylamine salt surfactants contains an average between about 16 and about 18 carbon atoms.

41. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein R of said alkoxyated quaternary alkylammonium salt surfactant(s) contains an average of between about 16 and about 18 carbon atoms.

42. A stable aqueous liquid herbicidal concentrate as set forth in claim 41 wherein R of said alkoxyated quaternary alkylamine salt surfactant is derived predominantly from tallow.

43. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the molar ratio of ammonium ions to glyphosate ions is at least about 1.2.

44. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the molar ratio of ammonium ions to glyphosate ions is at least about 1.5.

32

45. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the weight ratio of glyphosate, a.e., to the sum of alkoxyated quaternary alkylammonium salt(s) is between about 3 and about 20.

46. A stable aqueous liquid herbicidal concentrate as set forth in claim 45 wherein the weight ratio of glyphosate, a.e., to the sum of alkoxyated quaternary alkylammonium salt(s) is between about 3 and about 10.

47. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 wherein the concentration of the sum of alkoxyated quaternary alkylammonium salt surfactant(s) is between about 3 wt.% and about 12 wt.%.

48. A stable aqueous liquid herbicidal concentrate as set forth in claim 47 wherein the concentration of the sum of alkoxyated quaternary alkylammonium salt surfactant(s) is between about 3.5 wt.% to about 10 wt.%.

49. A stable aqueous liquid herbicidal concentrate as set forth in claim 23 having low eye toxicity.

50. A stable aqueous liquid herbicidal concentrate as set forth in claim 49 having a Red Band eye toxicity classification of yellow.

51. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 240 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.8 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant predominantly comprising an N-alkyl substituent derived from tallow.

52. A stable aqueous liquid concentrate as set forth in claim 51 wherein the weight ratio of the sum of all said alkoxyated alkyl quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) is greater than 4.5:1.

32
33

53. A stable aqueous liquid herbicidal concentrate as set forth in claim 51 comprising at least about 325 gpl glyphosate, a.e.

54. The stable aqueous liquid herbicidal concentrate of claim 23 comprising an ammonium salt of glyphosate and containing greater than 38.0 wt.% /L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.8 and about 2.5, at least one alkoxyated quaternary alkylammonium salt surfactant wherein each of p, q, p' and q' is independently an integer between 0 and 3,

said concentrate having a pH <7.3.

55. An aqueous liquid herbicidal concentrate as set forth in claim 54 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) is greater than 4:1.

56. The stable aqueous liquid herbicidal concentrate of claim 54, said concentrate having an ammonia concentration over the solution that is less than about 750 ppm at 25°C.

57. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 120 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.75 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_rR^5$ and B is $(R^6O)_p(R^7O)_q(R^8O)_rR^9$ where each of R², R³, R⁴, R⁵, R⁶, and R⁷ is independently selected from the group consisting of ethylene and isopropylene, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of [p + p' + q + q' + z + z'] is at least about 2,

the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and the molar concentration of alkoxyated quaternary alkylammonium ion in said aqueous concentrate being not greater than about 0.28.

58. A stable aqueous liquid concentrate as set forth in claim 57 wherein the molar concentration of said alkoxyated quaternary alkylammonium salt surfactant is not greater than about 0.25, 0.20, 0.15, 0.13, 0.10 or 0.08.

59. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 wherein R comprises between about 8 and about 18 carbon atoms.

60. A stable aqueous liquid herbicidal concentrate as set forth in claim 59 wherein R is predominantly derived from tallow.

61. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 wherein the weight ratio of the sum of all said alkoxyated alkyl quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) being greater than 4.5:1.

62. A stable aqueous liquid herbicidal concentrate as set forth in claim 61 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) being greater than 4.5:1.

63. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) being greater than 5.2:1.

64. A stable aqueous liquid herbicidal concentrate as set forth in claim 63 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) being greater than 5.2:1.

34
35

65. A stable aqueous liquid herbicidal concentrate as set forth in claim 63 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) being greater than 10:1.

66. A stable aqueous liquid herbicidal concentrate as set forth in claim 65 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) being greater than 10:1.

67. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 comprising at least about 240 gpl glyphosate, a.e.

68. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 comprising at least about 325 gpl glyphosate, a.e.

69. A stable aqueous liquid herbicidal concentrate as set forth in claim 68 comprising at least about 360 g/L glyphosate, a.e.

70. A stable aqueous liquid herbicidal concentrate as set forth in claim 69 comprising at least about 400 g/L glyphosate, a.e.

71. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 containing not more than about 5 wt.% ammonium sulfate.

72. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 3.25.

73. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 4.

36

74. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 having a Red Band eye toxicity classification of yellow.

75. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 wherein the molar concentration of alkoxyated quaternary alkylammonium ion is not greater than about 0.13.

76. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

77. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 120 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.75 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^5$ and B is $(R^6O)_p(R^7O)_q(R^8O)_zR^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $[p + p' + q + q' + z + z']$ is at least about 2,

the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and

the number average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 2 and about 10.

76
37

78. The stable aqueous liquid herbicidal concentrate of claim 57 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 3 and about 10, or between about 3 and about 8 or between about 4 and about 8 or between about 5 and 10.

79. An aqueous liquid herbicidal concentrate as set forth in claim 77 wherein the molar concentration of alkoxyated quaternary alkylammonium ion is not greater than about 0.28.

80. An aqueous liquid herbicidal concentrate as set forth in claim 77 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

81. A stable aqueous liquid herbicidal concentrate of claim 77 comprising at least two alkoxyated quaternary alkylammonium salt surfactants, wherein the average sum of $(p + p' + q + q' + z + z')$ for one of said at least two surfactants being between about 2 and about 5, and the average sum of $(p + p' + q + q' + z + z')$ for another of said at least two surfactants being between about 5 and about 15.

82. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the weight ratio of the sum of said one and said another surfactants to ammonium glyphosate, a.e., being between about 0.1:1 and about 0.2:1.

83. An aqueous liquid herbicidal concentrate as set forth in claim 82 wherein the weight ratio of said one surfactant to said another surfactant is between about 1:1.5 and about 1.5:1.

84. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the mole ratio of alkoxyated quaternary alkylammonium salt surfactant(s) to glyphosate is not greater than about 0.2:1.

85. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the weight ratio of alkoxyated quaternary alkylammonium salt surfactant(s) to glyphosate is between about 0.1:1 and about 0.17:1.

86. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the molar concentration of alkoxyated quaternary alkylammonium ion in said aqueous concentrate is not greater than about 0.15.

87. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2005/034076

A. CLASSIFICATION OF SUBJECT MATTER A01N57/20 A01N25/30 A01P13/00 //(A01N57/20,25:30)		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) A01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base used, when practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94/02021 A (MONSANTO COMPANY) 3 February 1994 (1994-02-03) page 2, line 23 - page 3, line 1 page 3, lines 22-36 page 4, lines 3-24, 34-37 page 6, lines 10-33 page 8, lines 2-19; examples 1-5 --- -/-	1-19, 23-87
☒ Further documents are listed in the compilation of Box C.		
☒ The patent family is as follows:		
* Special categories of cited documents:		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document not published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another claim or other special interest (see specification) *O* document relevant to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not so cited with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance: the claimed invention cannot be considered novel or inventive or considered to involve an inventive step unless the document is taken into account *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step unless the document is considered with one or more other such documents, each combination being obvious to a person skilled in the art *U* document member of the same patent family		
Date of the actual completion of the international search 27 January 2006		Date of mailing of the international search report 06/02/2006
Name and mailing address of the ISA/ European Patent Office, P.O. Box 16 Patentstr. 1 AL - 6800 Lausanne Tel. (+31-78) 240-2240, Tlx. 81 881 881 Fax (+31-78) 240-2212		Authorized officer Klaver, J

Form PCT/ISA/210 (second sheet) (April 2003)

28
39

INTERNATIONAL SEARCH REPORT

Patent application No.
PCT/US2005/034076

Documents considered to be relevant		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 998 332 A (SATO ET AL) 7 December 1999 (1999-12-07) cited in the application column 2, lines 1-35 column 3, lines 7-22, 38-50 column 4, lines 38-49 column 4, line 66 - column 5, line 7 column 5, line 48 - column 6, line 10 column 8, lines 17-19, 38-41 column 9, lines 35-57 column 10, lines 40-43 column 11, line 40 - column 12, line 9 column 15, lines 24-47; examples 1-7, 12, 19-21	1, 6-19, 23, 24, 29-62, 67-87
X	EP 0 582 561 A (MONSANTO COMPANY) 9 February 1994 (1994-02-09) page 3, lines 46-84 page 5, lines 17-24, 40-42; example 3	1-21
X	EP 0 274 369 A (MONSANTO COMPANY) 13 July 1988 (1988-07-13) page 2, lines 26-29 page 2, line 59 - page 3, line 22 page 3, lines 60-62; example I	1-13, 16-19
P, X	WO 2005/016002 A (DOW AGROSCIENCES LLC) 24 February 2005 (2005-02-24) page 3, lines 11-20 page 4, line 7 - page 5, line 12 page 10, lines 5-11, 20-22; example 1; table 1	1-10, 12, 13, 16-19
X	MYRILL J B ET AL: "GLYPHOSATE TOXICITY TO COMMON MILKWEED AND HEMP DOBBANE AS INFLUENCED BY SURFACTANTS" WEED SCIENCE, WEED SCIENCE SOCIETY OF AMERICA, CHAMPAIGN, IL, US, vol. 25, no. 3, May 1977 (1977-05), pages 276-287, XP002034447 ISSN: 0043-1745 page 278, column 1, paragraph 2 page 279, column 2, paragraph 1 table 5 page 284, column 1, paragraph 2; tables 7, 8	1-11, 13-15, 18, 19
-/-		

INTERNATIONAL SEARCH REPORT

Patent application No.
PCT/US2005/034076

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	P. E. LAERKE & J. C. STREIBIG: "Foliar absorption of some glyphosate formulations and their efficacy on plants" PESTIC. SCI., vol. 44, 1995, pages 107-116, XP009060636 page 108, column 1, paragraph 6 - column 2, paragraph 1; table 1 page 109, column 1, paragraph 1 page 111, column 1, paragraph 1 page 114, column 1, paragraph 1 page 114, column 2, paragraph 4	1-9, 11, 13-15
X	EP 0 526 444 A (MONSANTO COMPANY) 3 February 1993 (1993-02-03) page 2, line 43 - page 3, line 11 page 3, lines 45-58 page 4, lines 6-13, 43-50; examples 1-14	1-9, 11-13, 16, 17
X	US 5 462 912 A (HIOKI ET AL) 31 October 1995 (1995-10-31) column 2, line 64 - column 3, line 60 column 5, lines 10-27 column 6, lines 23-27 column 7, lines 62-67 column 9, lines 24-52; examples 1, 4, 5; tables 1A, 1B, 4A-5B	1-11, 13-22
X	WD 97/32476 A (KAO CORPORATION; MONSANTO COMPANY; OKANO, TETSUYA; HASEBE, KEIKO; SUZU) 12 September 1997 (1997-09-12) page 3, paragraph 2 page 7, paragraphs 2, 3 page 10, paragraph 4 - page 12, paragraph 1 page 14, paragraph 2 page 16, paragraph 2 compound (4) table 1 tables 3, 6-8	1, 2, 6-9, 11-14, 16, 17, 22

INTERNATIONAL SEARCH REPORT

section on patent family members

Patent application No.
PCT/US2005/034076

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9402021	A	03-02-1994	AT 179302 T AU 676432 B2 AU 4412193 A BR 9306732 A CA 2137281 A1 DE 69324683 D1 DE 69324683 T2 EP 0650326 A1 JP 7509700 T KR 169995 B1 MX 9304300 A1 NZ 253632 A US 5317003 A	15-05-1999 13-03-1997 14-02-1994 08-12-1998 03-02-1994 02-06-1999 25-11-1999 03-05-1995 26-10-1995 16-11-1998 31-01-1994 29-01-1997 31-05-1994
US 5998332	A	07-12-1999	AT 251383 T AU 732689 B2 AU 8582698 A BR 9810811 A CA 2297036 A1 CN 1115961 C DE 69818829 D1 DE 69818829 T2 DK 999749 T3 EP 0999749 A1 ES 2209171 T3 HU 0002407 A2 JP 2001510776 T NO 20000292 A NZ 502397 A PL 338233 A1 SK 772000 A3 TR 200000191 T2 TW 492843 B UA 66385 C2 WO 9904635 A1 ZA 9806502 A	15-10-2003 26-04-2001 16-02-1999 12-09-2000 04-02-1999 30-07-2003 13-11-2003 05-08-2004 16-02-2004 17-05-2000 16-06-2004 28-11-2000 07-08-2001 22-03-2000 26-04-2002 09-10-2000 14-08-2000 21-08-2000 01-07-2002 15-12-2000 04-02-1999 04-02-1999
EP 0582561	A	09-02-1994	AU 4432493 A CA 2101669 A1 JP 6256121 A NZ 248289 A US 5612285 A US 5693593 A	03-02-1994 01-02-1994 13-09-1994 24-02-1995 18-03-1997 02-12-1997
EP 0274369	A	13-07-1988	AU 595408 B2 AU 8204587 A DE 3764945 D1 DK 635087 A GR 3000911 T3 IE 61324 B1 JP 1983027 C JP 7002608 B JP 63145205 A KR 9200862 B1 NZ 222796 A	29-03-1990 09-06-1988 18-10-1990 05-06-1988 10-12-1991 02-11-1994 25-10-1995 18-01-1995 17-06-1988 30-01-1992 27-03-1990
WD 2005016002	A	24-02-2005	NONE	

From PCT/US2005/034076 (patent family member) (Page 2/2)

44
42

INTERNATIONAL SEARCH REPORT

Attention on patent family members

Inventor application No

PC1/US2005/034076

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0526444	A	03-02-1993	AT 146035 T 15-12-1996
		AU 648919 B2 05-05-1994	
		AU 2066192 A 04-02-1993	
		BR 9202963 A 30-03-1993	
		CA 2075004 A1 03-02-1993	
		DE 69215785 D1 23-01-1997	
		DE 69215785 T2 26-06-1997	
		JP 6024917 A 01-02-1994	
		MX 9204470 A1 01-05-1993	
		NZ 243780 A 23-12-1993	
		US 5430005 A 04-07-1995	
		ZA 9205731 A 05-11-1993	
US 5462912	A	31-10-1995	NONE
WO 9732476	A	12-09-1997	AU 713956 B2 16-12-1999
		AU 2231597 A 22-09-1997	
		BR 9702106 A 12-01-1999	
		CN 1190327 A 12-08-1998	
		DE 69713557 D1 01-04-2002	
		DE 69713557 T2 09-01-2003	
		EP 0824315 A1 25-02-1998	
		ES 2175349 T3 16-11-2002	
		ID 16129 A 04-09-1997	
		NZ 328990 A 29-06-1999	
		US 5948421 A 07-09-1999	

Form PCT/IB/210 (patent family members) (April 2003)

43

(12) SOLICITUD INTERNACIONAL PUBLICADA BAJO EL TRATADO DE COOPERACIÓN DE PATENTES (PCT)

(19) Organización Mundial de Propiedad
Intelectual
Oficina Internacional



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

(43) Fecha de Publicación Internacional
30 de Marzo de 2006 (30.03.2006)

PCT

(10) Número de Publicación Internacional
WO 2006/034426 A1

(51) Clasificación Internacional de Patentes: A01N 57/20,
25/30, A01P 13/00 // (A01N 57/20, 25:30)

(74) Agente: MANCINI, Ralph, J.; Akzo Nobel Inc.,
Intellectual Property Department, 7 Livingstone
Avenue, Dobbs Ferry, NY 10522-3408 (EU)

(21) Número de Solicitud Internacional:

PCT/US2005/034078

(81) Estados Designados (a menos que se indique lo
contrario, para todo tipo de protección nacional
disponible): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG,
BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE,
DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,
MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT,
RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(22) Fecha de Presentación Internacional:

23 de Septiembre 2004 (23.09.2004)

(25) Lengua de entrega: Inglés

(26) Lengua de Publicación: Inglés

(30) Datos de la Prioridad:
80/612,598 23 de Septiembre de 2004 (23.09.2004)
EU

(71) Solicitante (para todos los Estados designados
menos los Estados Unidos): AKZO NOBEL N.V.
[NL/NL]; Velperweg 76, 6824 BM Arnhem (NL).

(84) Estados Designados (a menos que se indique lo
contrario, para todo tipo de protección regional
disponible): ARIPO (BW, GH, GM, KE, LS, MW, MZ,
NA, SD, SL, SZ, TZ, UG, ZM, ZW), Euroasiática (AM,
AZ, BY, KG, KZ, MD, RU, TJ, TM), Europea (AT, BE,
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE,
IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR),
OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
MR, NE, SN, TD, TG).

(72) Inventores; e

(75) Inventores/Solicitantes (solo para los Estados
Unidos): ZHU, Shawn [EU/EU]; 132 Devon Farms
Road, Stormville, NY 12582 (EU). ABRAHAM,
William [IN/EU]; 17153 Lafayette Tralla Drive,
Wildwood, MO 63038 (EU). HEMMING-HAUS,
John [EU/EU]; Monsanto Company, 800 N.
Lindbergh Boulevard, ST. Louis, MO 63167 (EU).

Publicado:

— sin el informe de búsqueda internacional

— antes del vencimiento del tiempo límite para corregir las
reivindicaciones y a ser publicado nuevamente el recibir
tales correcciones.

Para códigos de dos letras y otras abreviaciones, referirse a
las "Notas de guía sobre Códigos y Abreviaturas" que
aparecen al comienzo de cada edición de la Gaceta del PCT.

(54) Título: AGENTES TENSIOACTIVOS DE ALQUILAMINA CUATERNARIA ALCOXILADA PARA
GLIFOSATO

(57) Resumen: La presente invención está relacionada con formulaciones de glifosato estable con eficacia
mejorada por surfactante de alquilamina cuaternario alcoxilado de alta efectividad a un nivel usado muy bajo. El
surfactante de alquilamina cuaternario alcoxilado es compatible con todas las sales de las formulaciones del
glifosato (Incluyendo potasio y amonio) AÚN A MUY ALTAS CONCENTRACIONES (470 – 600 g a.e./l).

AGENTES TENSIOSCTIVOS DE ALQUILAMINA CUATERNARIA
ALCOXILADA PARA GLIFOSATO

CAMPO DE LA INVENCION

5

La presente invención se refiere a las formulaciones de glifosato que comprenden agentes tensioactivos cuaternarios de alquilamina alcoxilada que tienen actividad herbicida mejorada.

10

ANTECEDENTES DE LA INVENCION

N-fosfonometilglicina, de otra manera conocida como glifosato, se conoce bien en la técnica como un herbicida efectivo aplicado después del surgimiento foliar. El glifosato es un compuesto orgánico con tres grupos ácidos, y en su forma ácida es relativamente insoluble en agua. Por lo tanto, el glifosato normalmente se formula y se aplica como una sal soluble en agua. Aunque se pueden elaborar sales de glifosato monobásicas, dibásicas y tribásicas, generalmente se prefiere formular y aplicar el glifosato, en la forma de una sal monobásica, por ejemplo como una sal de mono-isopropilamina, mono- potasio o mono-amonio, o una sal dibásica tal como la sal de diamonio. Se conocen las formulaciones del herbicida glifosato las cuales comprenden efectivamente una mezcla de sales de mono-amonio y di-amonio, por ejemplo,

en donde la relación molar del ión de amonio al anión de glifosato en la formulación se encuentra entre 1 y 2.

Cuando los términos "amonio", "monoamonio" y "diamonio" se utilizan en la presente invención para referirse a sales de glifosato, estos términos se aplican estrictamente al amonio inorgánico, por ejemplo, NH_4^+ , a menos que el contexto lo demande otra manera. Las relaciones y concentraciones del glifosato dadas en la presente invención, incluso cuando el glifosato está presente como una sal o como sales, se expresan como equivalentes ácidos (a.e. - por sus siglas en inglés) a menos que el contexto lo demande otra manera.

Para muchas aplicaciones, las sales de glifosato requieren la presencia de un agente tensioactivo adecuado para un mejor desempeño que herbicida. El agente tensioactivo se puede proveer ya sea en la forma de un concentrado, o se puede añadir por el usuario final a la solución para aspersión diluida. La elección del agente tensioactivo puede ser importante puesto que existen amplias variaciones entre los agentes tensioactivos en su capacidad para mejorar la eficiencia herbicida del glifosato para aplicaciones particulares.

Es ventajoso el uso de una formulación acuosa altamente concentrada de glifosato en la forma de una sal elaborada con la base inorgánica de amoniaco y potasio. El amoniaco y el potasio son fácilmente disponibles, tienen bajos pesos moleculares, y son relativamente solubles en agua. Adicionalmente, estos son nutrientes naturales para el crecimiento de

plantas y otros organismos. Sin embargo, el uso de sales de amonio y de potasio del glifosato para la preparación de formulaciones concentradas acuosas del glifosato adecuadas para eliminar y controlar malezas y otras plantas se ha limitado debido a dificultades que se generan por las propiedades químicas y físicas de las sales de amonio y de potasio del glifosato, a la ausencia de agentes tensioactivos adecuados para la preparación de concentrados líquidos altamente cargados de dichas sales, al reducido control de malezas, y al requerimiento de procesos complejos para la preparación de composiciones líquidas de amonio y potasio del glifosato.

Por consiguiente, es deseable desarrollar una formulación acuosa de glifosato (i) que tenga una alta carga de glifosato a.e., (ii) que contenga un agente tensioactivo adecuado que mejore la eficiencia herbicida que se puede utilizar para todas las sales de glifosato, y (iii) que tenga una concentración optimizada a un nivel de carga muy bajo de ese agente tensioactivo para proveer una mayor efectividad herbicida en comparación con las formulaciones estándares comerciales de sales de glifosato.

Por lo tanto, es un objetivo de la presente invención el proveer una formulación acuosa altamente concentrada, estable al almacenamiento que contiene glifosato junto con uno o más agentes tensioactivos aceptables en el área de la agricultura que mejoran la efectividad herbicida de las aplicaciones de la formulación.

Es un objetivo adicional de la presente invención el proveer una formulación acuosa altamente concentrada, estable al almacenamiento que

27
48

contiene glifosato y uno o más agentes tensioactivos y que tiene un nivel superior de efectividad herbicida mediante comparación con las formulaciones actuales estándares comerciales de sales de glifosato.

Existe una necesidad particular en la técnica por formulaciones

5 líquidas acuosas estables que comprenden un agente tensioactivo de la sal del amonio cuaternario tales como, por ejemplo, un haluro dialquilamonio dialcoxilado, y en particular por formulaciones que comprenden amonio de glifosato y un agente tensioactivo de sal de dialquilamonio dialcoxilado. Dichas formulaciones se conocen en la técnica, pero generalmente se requiere una

10 fracción significativa de agente tensioactivo no iónico para mantener la estabilidad de la formulación. Adicionalmente, la sal de amonio cuaternario en muchas de esas formulaciones comprende el di(hidroxietil)metil cocoamino, el cual es altamente efectivo

15

BREVE DESCRIPCION DE LA INVENCION

La presente invención se refiere a las formulaciones de glifosato que tienen una estabilidad mejorada y bioeficiencia que comprenden como un adyuvante, al menos un agente tensioactivo cuaternario de alquilamina

20 alcoxilada. El adyuvante anteriormente mencionado se puede emplear a relaciones de dosis bajas y es estable en todas las diversas sales de glifosato incluso a una concentración muy alta.

DESCRIPCION DETALLADA DE LA INVENCION

Las formulaciones de glifosato generalmente requieren uno o más adyuvantes con el objeto de reforzar su bio-eficiencia. La cantidad de adyuvante empleado es típicamente una relación de glifosato ácido: adyuvante de aproximadamente 3:1 a 5:1 o menor con el objeto de lograr un efecto significativo de refuerzo. Los costos asociados con el uso de los adyuvantes y otros aditivos en las formulaciones de glifosato pueden ser significativos. Por lo tanto, existe una necesidad creciente para encontrar un adyuvante más efectivo y económico para el glifosato.

El glifosato es un ácido con una solubilidad muy limitada en agua mientras que las sales de glifosato tienen una solubilidad muy alta en agua. Por lo tanto, las formulaciones de glifosato usualmente emplean sales de glifosato. Se han utilizado muchos contraiones comercialmente en los productos de glifosato. Estos incluyen isopropilamina, monoetanolamino, sodio, trimetilsulfonio, potasio, y amonio. Por consiguiente, existen numerosas sales de glifosato, y muchas más elecciones de agente tensioactivo utilizado en las formulaciones. Sin embargo, el uso de demasiados agentes tensioactivos en una formulación vegetal de glifosato puede crear problemas de logística en parte debido al hecho de que se requieren recipientes de almacenamiento separados para cada agente tensioactivo. Esto puede ser costoso, y por lo tanto existe una necesidad para minimizar el número de agentes tensioactivos en una formulación vegetal de glifosato.

Para las formulaciones líquidas concentradas de glifosato, una carga práctica de glifosato puede ser de 360 g a.e./l o mayor. Se sabe por un experto en la técnica que no se pueden incorporar agentes tensioactivos biológicamente útiles en las formulaciones de glifosato sin separación de fase

5 en la carga práctica del glifosato y de los agentes tensioactivos, en particular en el caso de las sales de potasio y de amonio. Por lo tanto, uno de los objetivos es encontrar un agente tensioactivo altamente eficiente que se pueda utilizar a niveles muy bajos en las formulaciones de glifosato para mejorar la bioeficiencia del glifosato en donde el agente tensioactivo se puede

10 formular en un formulaciones concentradas líquidas estables que contiene glifosato como las sales de potasio o de amonio a 470 - 600 g a.e./l.

La presente invención satisface este objetivo al proveer formulaciones de glifosato que tienen estabilidad mejorada y bioeficiencia que comprenden, como un adyuvante, al menos un agente tensioactivo

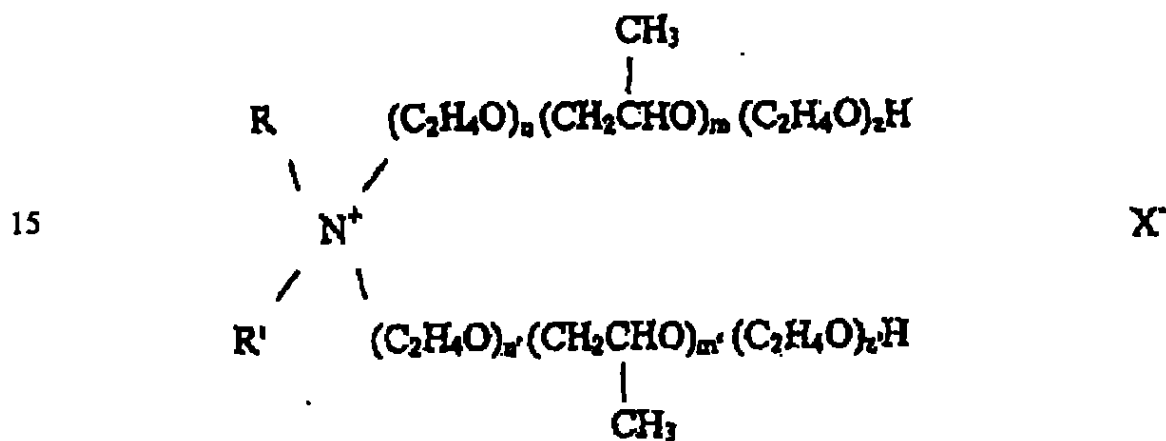
15 cuaternario de alquilamina alcoxilada. El adyuvante anteriormente mencionado se puede emplear a relaciones de dosis bajas y es estable en todas las diversas sales de glifosato incluso a una concentración muy elevada de glifosato. A este respecto, se ha descubierto de manera inesperada que una clase de agentes tensioactivos ejemplificados por los agentes

20 tensioactivos cuaternarios de cocoamino con 2EO a un nivel de uso de 3% (cantidad activa) mejoran significativamente la eficiencia de las formulaciones de glifosato en el control de malezas no deseadas. Se encontró que son más efectivos que los productos comerciales conocidos y que se pueden



incorporar a una carga muy elevada de hasta 600 g a.e./l de glifosato de potasio y 470 g a.e./l de glifosato de amonio. A concentración están elevadas como 600 g a.e./l de glifosato de potasio y 470 g a.e./l de glifosato de amonio, varios de los agentes tensioactivos utilizados en los productos comerciales habituales de glifosato ocasionarán que se separen las fases de la formulación. Además, los agentes tensioactivos cuaternarios de cocoamino-2EO son compatibles con todas las diversas sales de glifosato, incluso a una carga muy elevada.

La clase de adyuvantes agentes tensioactivos cuaternarios de alquilamina alcoxilada de conformidad con la presente invención se representa por la fórmula general I, a continuación:



en donde R es un grupo alquileo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono; R' es un grupo alquileo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono; y $n+n'$ es un entero de 0-30, $m + m'$ es un entero de 0 a 30, y $z + z'$ es un entero de 0-30, con la condición de que $n + z$

SX
52

es al menos 1 y/o $n' + z'$ es al menos 0 ó 1, y X- es un anión compatible tal como metil sulfato o Cl-. En una modalidad preferida, el grado de etoxilación es al menos 1 y de hasta 30. Alternativamente, los grupos etoxi terminales pueden estar modificados en el extremo con, por ejemplo, un grupo metilo o etilo.

Un agente tensioactivo catiónico preferido es cloruro de metil bis(2-hidroxietil)coco amonio. En ciertas composiciones preferidas de la invención el agente tensioactivo catiónico es cloruro de metil bis(2-hidroxietil)cocoamonio y no existe una cantidad significativa de agente tensioactivo no iónico secundario empleada en la formulación. Los agentes tensioactivos no iónicos tales como polioxoetilen alquiléter incluyendo polioxoetilen alcohol secundario tienen un promedio de aproximadamente 3 a aproximadamente 15 moles de óxido de etileno a una concentración mayor de 5% con una relación de catiónicos a no iónicos menor de 5.2, que se excluye específicamente a partir de las formulaciones de la presente invención.

En otra modalidad, la formulación de la invención contiene menos de aproximadamente 0.5% en peso de otros agentes tensioactivos; en otra modalidad menos de aproximadamente 0.2% en peso de otros agentes tensioactivos; en otra modalidad menos de aproximadamente 0.1% de otros agentes tensioactivos, y en incluso otra modalidad no existen cantidades sustanciales de otros agentes tensioactivos.

Las formulaciones concentradas solubles en agua de la presente invención típicamente contendrán una cantidad de agente tensioactivo de

aproximadamente 0.5% a aproximadamente 10% en peso en total de uno o más agentes tensioactivos. Preferiblemente se utiliza de aproximadamente 2% a aproximadamente 8% en peso de agente tensioactivo aunque si se desea se pueden emplear cantidades mayores o menores. Las cantidades y

5 clases de agente tensioactivo utilizado en las composiciones de la presente invención se seleccionan para proveer altos niveles de eficiencia herbicida y una mezcla homogénea estable en fase particular en el caso de una formulación líquida. La invención también se aplica a formulaciones sólidas.

Una composición de la invención puede comprender

10 opcionalmente otros aditivos tales como sulfato de amonio, sulfato de potasio, cloruro de potasio, sulfato de sodio, urea, o mezclas de los mismos. Una composición contemplada puede incluir opcionalmente un agente sinérgico, un aditivo para quemadura rápida, un humectante, un co-herbicida, un colorante, un pigmento, un inhibidor de la corrosión, un espesante, un agente

15 para dispersión, un secuestrador de calcio, un agente para evitar la formación espuma, un anticongelante, un depresivo por puntos, o mezclas de los mismos. Preferiblemente, los aditivos utilizados en las composiciones de la presente invención poseen una solubilidad o dispersión adecuada en una solución acuosa concentrada de glifosato para permitir que se produzcan las

20 concentraciones deseadas.

En donde se incluye un co-herbicida en la formulación, es preferible que el co-herbicida sea soluble en agua. Los ejemplos de co-herbicidas adecuados son las sales de sulfonilurea, glufosinato, acifluorfen,

asulam, benazolin, bentazon, bialaphos, bromacil, bromoxinil, cloramben, clopiralid, 2,4-D, 2,4-DB, dalapon, dicamba, diclorprop, diclofop, diquat, endothall, fenac, fenoxaprop, flamprop, fluazifop, fluoroglicofen, fomesafen, fosamino, haloxifop, imazameth, imazamethabenz, imazamox, imazapir, 5 imazaquin, imazethapir, ioxinil, MCPA, MCPB, mecoprop, ácido metilarsónico, naptalam, ácido nonanóico, paraquat, picloram, ácido sulfámico, 2,3,6-TBA, TCA y triclopir. Un co-herbicida preferido es sal IPA de 2,4-D. Alternativamente, se puede seleccionar al menos un compuesto herbicidamente activo empleado a partir del grupo anteriormente mencionado, 10 con o sin la inclusión de glifosato.

Uno o más auxiliares del procesamiento conocidos por los expertos en la técnica también se pueden emplear en las formulaciones de la presente invención. Los glicoles son un auxiliar de procesamiento preferido. Los glicoles preferidos incluyen, pero no se limitan a propilen glicol, dietil 15 glicol, etilen glicol, dipropilen glicol, mezclas de los mismos y los similares. Un ejemplo de una composición de la invención contiene glifosato de amonio en una cantidad de aproximadamente 450 a aproximadamente 500 g a.e./l, junto con de aproximadamente 3% a aproximadamente 5.2% en peso del cloruro de metil bis(2-hidroxietil)cocoamonio, y de aproximadamente 0.75% a 20 aproximadamente 1.6% en peso del dietilen glicol. No se emplea agente tensioactivo no iónico.

Las formulaciones de la presente invención también se pueden preparar generalmente mediante la mezcla del glifosato técnico, junto con

otros ingredientes en un recipiente adecuado para mezcla con agitación, tal como una mezcladora. El calentamiento puede ser necesario para facilitar el mezclado.

Esta invención también se refiere a un método herbicida para el uso de una composición contemplada en una cantidad efectiva para eliminar o controlar vegetación no deseada mediante la dilución de la composición en agua y aplicando la composición diluida al follaje de la vegetación a ser eliminada o controlada.

Las formulaciones de glifosato, como se formulan en una composición de la invención, se deben aplicar al follaje vegetal a una relación de aplicación adecuado para producir el efecto deseado. Las relaciones de aplicación usualmente se expresan como cantidad de glifosato a.e. por unidad de tierra tratada, por ejemplo gramos a.e. per hectárea (g a.e./ha). Lo que constituye un "efecto deseado" varía de conformidad con los estándares y práctica de aquellos que investiguan, desarrollan, comercialicen y utilizan los productos de glifosato. Por ejemplo, la cantidad de glifosato a.e. aplicado por unidad diaria para producir, de manera consistente y confiable, al menos 85% de control de una especie vegetal como se mide por la reducción del crecimiento o la mortalidad frecuentemente se utiliza para definir una relación comercialmente efectiva.

Las composiciones preferidas de la invención proveen efectividad herbicida mejorada en comparación con formulaciones comerciales estándares de glifosato "efectividad herbicida", como se utiliza en

56

la presente invención, se refiere a cualquier medida observable del control del crecimiento vegetal, que puede incluir una o más de las acciones de (1) eliminar, (2) inhibir el crecimiento, reproducción o proliferación, y (3) remover, destruir, o disminuir de otra manera la presencia y actividad de las plantas.

5 La selección de relaciones de aplicación que son biológicamente efectivas para una formulación específica de glifosato, tal como una formulación de la presente invención, se encuentra dentro de la capacidad del científico común con conocimientos en agricultura. De manera similar, aquellos expertos en la técnica reconocerán que las condiciones de la planta
10 individual, clima y condiciones de crecimiento, así como la formulación específica seleccionada, influirán el grado de efectividad biológica alcanzado en la práctica de esta invención. Las relaciones de aplicación útiles pueden depender por lo tanto, de todas las condiciones anteriormente mencionadas. Se tiene mucha información acerca de las relaciones de aplicación apropiadas
15 para las formulaciones de glifosato en general. En dos décadas de uso de glifosato y de estudios publicados en relación con dicho uso se ha provisto abundante información a partir de la cual un practicante para el control de malezas puede seleccionar las relaciones de aplicación de glifosato que son herbicidamente efectivas en especies particulares en etapas de crecimiento
20 particulares en condiciones ambientales particulares.

Se pueden emplear diversos métodos de aplicación incluyendo aspersión general, aspersión dirigida o limpieza del follaje con una composición diluida de la invención. Dependiendo del grado de control

SB
57

deseado, la edad y especies de las plantas, condiciones ambientales y otros factores, típicamente la relación de aplicación de glifosato es una cantidad herbicidamente efectiva de aproximadamente 0.1 a aproximadamente 10 kg a.e./ha y preferiblemente de aproximadamente 0.25 a aproximadamente 2.5 kg a.e./ha, aunque se pueden emplear cantidades mayores y menores.

Las composiciones herbicidas de glifosato o derivados de las mismas se utilizan para controlar una amplia variedad de plantas a nivel mundial. Las composiciones de glifosato de la invención se pueden aplicar a una planta en una cantidad herbicidamente efectiva, y pueden controlar de manera efectiva una o más especies vegetales de uno o más de los siguientes géneros sin restricción: 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, Malva, Oryza, Ottochloa, Panicum, Paspalum, Phalaris, Phragmites, Polygonum, Portulaca, Pteridium, Pueraria, Rubus, Salsola, Setaria, Sida, Sinapis, Sorghum, Triticum, Typha, Ulex, Xanthium y Zea.

Las especies de hojas anchas anuales particularmente importantes para las cuales se utilizan las composiciones de glifosato se ejemplifican sin limitación por las siguientes: hoja de terciopelo (Abutilon theophrasti), amaranto (Amaranthus spp.), buttonweed (Borreria spp.), semilla oleosa de colza, canola, mostaza de la india, etc. (Brassica spp.), commelina (Commelina spp.), filaree (Erodium spp.), girasol (Helianthus spp.), gloria

57
58

matutina (*Ipomoea* spp.), kochia (*Kochia scoparia*), malva (*Malva* spp.), buckwheat silvestre, smartweed, etc. (*Polygonum* spp.), purslane (*Portulaca* spp.), russian thistle (*Salsola* spp.), sida (*Sida* spp.), mostaza silvestre (*Sinapis arvensis*) y cocklebur (*Xanthium* spp.)

- 5 Las especies de hojas estrechas anuales particularmente importantes para las cuales se utilizan las composiciones de glifosato se ejemplifican sin limitación por las siguientes: avena silvestre (*Avena fatua*), césped alfombra (*Axonopus* spp.), downy brome (*Bromus tectorum*), crabgrass (*Digitaria* spp.), barmyardgrass (*Echinochloa crus-galli*), goosegrass
- 10 (*Eleusine indica*), annual ryegrass (*Lolium multiflorum*), arroz (*Oryza sativa*), ottochloa (*Ottochloa nodosa*), césped bahía (*Paspalum notatum*), canarygrass (*Phalaris* spp.), con la de zorro (*Setaria* spp.), trigo (*Triticum aestivum*) y maíz (*Zea mays*).

- Las especies de hojas anchas perennes particularmente
- 15 importantes para las cuales se utilizan las composiciones de glifosato se ejemplifican sin limitación por las siguientes: mugwort (*Artemisia* spp.), milkweed (*Asclepias* spp.), canada thistle (*Cirsium arvense*), field bindweed (*Convolvulus arvensis*) y kudzu (*Pueraria* spp.).

- Las especies de hojas estrechas perennes particularmente
- 20 importantes para las cuales se utilizan las composiciones de glifosato se ejemplifican sin limitación por las siguientes: brachiaria (*Brachiaria* spp.), césped de Bermudas (*Cynodon dactylon*), yellow nutsedge (*Cyperus esculentus*), purple nutsedge (*C. rotundus*), quackgrass (*Elymus repens*),
-

E
B
59

lalang (*Imperata cylindrica*), césped de centeno perenne (*Lolium perenne*), césped de Guinea (*Panicum maximum*), dallisgrass (*Paspalum dilatatum*), reed (*Phragmites* spp.), césped johnson (*Sorghum halepense*) y cattail (*Typha* spp.).

- 5 Otras especies perennial particularmente importantes para las cuales se utilizan las composiciones de glifosato se ejemplifican sin limitación por las siguientes: cola de caballo (*Equisetum* spp.), bracken (*Pteridium aquilinum*), mora (*Rubus* spp.) y gorse (*Ulex europaeus*).

- 10 Por lo tanto, las composiciones de glifosato de la presente invención, y un método para el tratamiento de plantas con dichos composiciones, pueden ser útiles para cualesquiera de las especies anteriormente mencionadas. En un método de uso particular contemplado, una composición de la invención que comprende glifosato y agente tensioactivo se aplica al follaje de las plantas de cosechas genéticamente
- 15 transformadas para tolerar el glifosato, y simultáneamente al follaje de las malezas o plantas no deseadas que crecen en proximidad cercana a dichos plantas de cosechas. Este proceso resulta en el control de las malezas o de las plantas no deseadas mientras que deja a las plantas de cosechas sustancialmente sin daños.

- 20 La aplicación de composiciones diluidas al follaje de las plantas preferiblemente se lleva a cabo mediante aspersión, utilizando medios convencionales para asperjar líquidos, tales como boquillas para aspersión, atomizadores, o los similares. Las composiciones de la presente invención se
-

pueden utilizar en técnicas de cultivo de precisión, en la cual se emplea un instrumento para variar la cantidad del glifosato aplicado a las diferentes partes de un campo, dependiendo de variables tales como las especies vegetales particulares presentes, composición del suelo, y los similares. En una modalidad de dichas técnicas, se pueden utilizar un sistema de posicionamiento global operado con el aparato para aspersión para aplicar la cantidad deseada de una composición diluida a las diferentes partes de un campo.

Una composición de la invención preferiblemente se diluye hasta un grado adecuado en agua para que se pueda asperjar fácilmente utilizando equipo estándar para aspersión de uso en agricultura. La relación por unidad de área de tierra de la composición diluida mediante aspersión convencionalmente se conoce como "volumen de aspersión". Los volúmenes de aspersión adecuados para la presente invención pueden variar dependiendo de numerosos factores, incluyendo las especies vegetales involucradas. Los volúmenes útiles para aspersión para la aplicación de una composición diluida de la invención al follaje pueden tener un intervalo de aproximadamente 25 a aproximadamente 1,000 litros por hectárea (l/ha), preferiblemente de aproximadamente 50 a aproximadamente 300 l/ha.

Las formulaciones particularmente preferidas de la invención comprenden concentrados líquidos acuosos estables que comprenden una sal amonio o diamonio de glifosato y un agente tensioactivo de sal de alquilamonio cuaternario alcoxilado. Las formulaciones que contienen sales de

diamonio de glifosato son particularmente preferidas. Generalmente, la relación molar del ión de amonio con respecto al ión de glifosato en la formulación puede tener un intervalo de aproximadamente 0.8 a aproximadamente 2.5. Se prefiere una relación del ión de amonio con respecto al ión de glifosato de al menos aproximadamente 1.2. Las relaciones del ión de amonio con respecto al ión de glifosato entre aproximadamente 1.5 y aproximadamente 2.2 pueden ser particularmente ventajosas para algunas aplicaciones. Preferiblemente, la formulación contiene al menos aproximadamente 120 g/L, más preferiblemente al menos aproximadamente 240 g/L, 300 g/L o 325 g/L, e incluso más preferiblemente al menos aproximadamente 360 g/L de glifosato, a.e. En ciertas modalidades, el contenido de glifosato a.e., puede ser mayor de aproximadamente 400 g/L, mayor de aproximadamente 425 g/L o mayor de aproximadamente 450 g/L. El agente tensioactivo puede corresponder a la fórmula anteriormente establecida, o más generalmente a la fórmula:



en donde R es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, A es $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ y B es $(R^5O)_{p'}(R^6O)_{q'}(R^7O)_zR^9$ en donde cada uno de R^2 , R^3 , R^4 , R^5 , R^6 , y R^7 se selecciona independientemente a partir del grupo que consiste de etileno e isopropileno, cada uno de R^8 y R^9 se selecciona independientemente a partir

de hidrógeno, metilo y etilo, y cada uno de p , q , p' , q' , z y z' es independientemente un entero entre 0 y 30 y $p + p' + q + q' + z + z'$ es al menos aproximadamente 2.

La relación en peso de la suma de todos esos agente(s) tensioactivo(s) de sal de alquilamonio cuaternario alcoxilado con respecto a la suma de cualquier agente tensioactivo(s) de alquil éter de óxido de polialquileo típicamente es mayor de 4.5:1, preferiblemente mayor de aproximadamente 5.2:1, e incluso más preferiblemente mayor de aproximadamente 10:1 o 20:1. En ciertas modalidades especialmente preferidas, el concentrado de glifosato de amonio carece sustancialmente de cualquier agente tensioactivo de alquil éter de óxido de polialquileo, por ejemplo, la concentración del último tipo de agente tensioactivo es una continuación el nivel en el cual éste tiene cualquier efecto funcional como un agente tensioactivo y/o una continuación del nivel en el cual éste tiene cualquier efecto mensurable en el punto de opacidad de la formulación. También se prefiere que la relación en peso de la suma de todos esos agentes tensioactivo de la sal de alquilamonio cuaternario alquil alcoxilado con respecto a la suma de todos los agentes tensioactivo no iónicos sea mayor de aproximadamente 4.5:1, más preferiblemente mayor de aproximadamente 5.2:1, e incluso más preferiblemente mayor de aproximadamente 10:1 ó 20: 1. De manera ventajosa, el concentrado de glifosato de amonio puede carecer sustancialmente de cualquier agente tensioactivo no iónico, "carecer sustancialmente" siendo entendido como se describió anteriormente.

67
63

Para muchas aplicaciones, se prefiere que la suma de $(p + p' + q + q' + z + z') = 2$, por ejemplo, que el agente tensioactivo sea un 2EO dialquilamonio u otra sal de bis(hidroxicuil)dialquilamonio tal como bis(hidroxietyl)metil-cocoamino o bis(hidroxietyl) metilseboamino. Para otras

5 aplicaciones, se puede preferir que $(p + p' + q + q' + z + z') > 3$. En donde las sal cuaternaria de alquilamonio se prepare mediante la alcoxilación más allá de las especies bis(hidroxicuil), el agente tensioactivo obtenido típicamente es una mezcla de homólogos con un grado variable de alcoxilación. Dichos

10 agentes tensioactivos se pueden caracterizar mejor mediante el número promedio del valor de $(p + p' + q + q' + z + z')$, algunas veces referido en la presente invención como W_0 . Por ejemplo, los agentes tensioactivos de alquilamonio cuaternario alcoxilado para algunas aplicaciones pueden tener un valor W_0 número promedio entre aproximadamente 3 y aproximadamente

15 7, o más particularmente entre aproximadamente 4 y aproximadamente 6. En otros casos, una sal de alquilamonio cuaternario alcoxilado puede tener un valor W_0 entre aproximadamente 6 y aproximadamente 15, o más particularmente entre aproximadamente 8 y aproximadamente 12. Algunas

20 formulaciones pueden comprender combinaciones de agentes tensioactivos de alquilamonio cuaternario alcoxilado, por ejemplo, un agente tensioactivo que tiene un valor relativamente bajo de W_0 , por ejemplo de aproximadamente 2, o en el intervalo de 3 a 7, y otro agente tensioactivo que tiene un valor relativamente elevado de W_0 , por ejemplo, en el intervalo de

aproximadamente 8 a aproximadamente 15 o entre aproximadamente 8 y aproximadamente 12.

En ciertas modalidades preferidas de la invención, el agente tensioactivo de sal de dialquilamonio cuaternario alcoxlado comprende una
5 mezcla de homólogos en donde R contiene un promedio de entre aproximadamente 16 y aproximadamente 18 átomos de carbono. En ciertas modalidades particularmente preferidas, R se deriva a partir de sebo.

Se ha encontrado que los concentrados líquidos acuosos estables que comprenden agentes tensioactivos de sal de glifosato de
10 diamonio y de sal de dialquilamonio cuaternario alcoxlado se pueden formular a concentraciones en exceso de 38.0% en peso de glifosato, a.e., y que dichos concentrados pueden exhibir un pH menor de 7.3 y una concentración de amoniaco en la solución de menos de aproximadamente 750 ppm a 25°C.

En las formulaciones de glifosato de amonio de la invención, las
15 relaciones en peso del glifosato, a.e., con respecto a las sal de alquilamonio cuaternario alcoxlado típicamente se encuentran entre aproximadamente 3 y aproximadamente 20, + típicamente entre aproximadamente 3 y aproximadamente 10. Las formulaciones particularmente adecuadas de glifosato de diamonio se pueden preparar para que tengan una relación de
20 glifosato con respecto al agente tensioactivo de sal de alquilamonio cuaternario alcoxlado de entre aproximadamente 3.5 a aproximadamente 9. Expresado con base en el concentrado total, la concentración de la suma del agente(s) tensioactivo(s) de sal de alquilamonio cuaternario alcoxlado

típicamente puede tener un intervalo de aproximadamente 3% en peso a aproximadamente 12% en peso, más típicamente de aproximadamente 3.5% en peso a aproximadamente 10% en peso.

El concentrado preferido de glifosato de amonio de la invención
5 también se puede formular sin proporciones sustanciales ya sea de sulfato de amonio o de un alquilen glicol tal como etilen glicol o propilen glicol, o un alquilen éter glicol tal como dietilen glicol.

Por ejemplo, el contenido de sulfato de amonio puede ser menor de aproximadamente 5% en peso, menor de aproximadamente 3% en peso,
10 menor de aproximadamente 2% en peso o menor de aproximadamente 1% en peso. De hecho, el concentrado puede estar sustancialmente carente de sulfato de amonio.

De manera similar, la relación en peso de la suma del agente tensioactivo de sal de dialquilamonio cuaternario alcoxilado con respecto al
15 alquilen glicol y/o al alquilen éter glicol puede ser mayor de aproximadamente 3.25, y preferiblemente es mayor de aproximadamente 4, típicamente mayor de aproximadamente 5, y más típicamente mayor de aproximadamente 6, 8 ó 10. La relación de la suma del agente tensioactivo de sal de dialquilamonio cuaternario alcoxilado con respecto a la suma de (todos los agentes
20 tensioactivos de alquil éter de óxido de polialquileno + alquilen glicoles + alquilen éter glicoles) es mayor de aproximadamente 2, preferiblemente mayor de aproximadamente 3, típicamente mayor de aproximadamente 5, 8 ó 10.

65
66

Los agentes tensioactivos de alquil éter de óxido de polialquileno se han utilizado para limitar la toxicidad al ojo de los concentrados de sal de glifosato que comprenden agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado, mientras que los alquylene glicoles y alquilen éter glicoles típicamente se presentan en los concentrados de glifosato que comprenden sal de alquilamonio cuaternario alcoxlado y en los agentes tensioactivos de alquil éter de óxido de polioxietileno. Se ha descubierto que los concentrados de glifosato de amonio de la presente invención se pueden formular con concentraciones mínimas de agentes tensioactivos no iónicos, concentraciones mínimas de alquylene éter glicoles, concentraciones mínimas de alquylene éter glicoles, o con concentraciones mínimas de cualesquiera agentes tensioactivo iónicos, alquilen glicoles, o alquilen éter glicoles. Ciertas formulaciones preferidas pueden estar sustancialmente carentes de cada uno, de cualquiera, y/o de todos estos.

La ausencia o ausencia sustancial de alquil éter de óxidos de polialquileno y otros elementos no iónicos contribuyen a la estabilidad de las formulaciones, debido a que los agentes tensioactivos no iónicos pueden comprometer la estabilidad de los concentrados de glifosato de amonio que comprenden agentes tensioactivos de sal de alquilamonio alcoxlado de conformidad con la invención, se ha descubierto que los concentrados de glifosato de diamonio que contienen, por ejemplo, 2EO, 5 EO y 10 EO metilcocoquats y metiltallowquats se pueden formular sin cualquier agente tensioactivo no iónico, un alquilen glicol, o un alquilen éter glicol.

35
67

Además, de conformidad con la invención, se ha descubierto que los concentrados acuosos líquidos de glifosato de amonio que tienen una toxicidad sorprendentemente baja para el ojo se pueden formular con concentraciones mínimas de alquil éter de óxido de polialquileño u otros agentes tensioactivos no iónicos. De hecho, se ha encontrado que dichas formulaciones con baja toxicidad al ojo pueden estar sustancialmente carentes de agentes tensioactivos no iónicos. Antes de la presente invención, se había entendido que, para satisfacer los estándares de toxicidad al ojo de al menos ciertas jurisdicciones sin incorporar una fracción significativa de agente tensioactivo, la concentración de agentes tensioactivos catiónicos en los concentrados de glifosato de amonio se debían mantener a niveles significativamente bajos en comparación con aquellos deseados para la eficiencia herbicida. Por ejemplo, se había entendido que, en un concentrado de glifosato de amonio que tenía una mayor carga de aproximadamente 360 g/L de glifosato, a.e., la concentración total de los agente(s) tensioactivo(s) de sal de alquilamonio cuaternario dialcoxilado se debían mantener a no más de aproximadamente 3.5% en peso, preferiblemente no más de aproximadamente 3.2% en peso, y/o que la relación en peso de dicho agente tensioactivo(s) con respecto al glifosato, a.e., no debía ser mayor de aproximadamente 0.28, preferiblemente no mayor de aproximadamente 0.25, típicamente no mayor de aproximadamente 0.20, 0.15, 0.13, 0.10 o 0.08. Sin embargo, de conformidad con la invención, se ha encontrado que una baja toxicidad al ojo se puede preservar a una concentración de agente

tensioactivo significativamente mayor cuando ciertos principios novedosos se observan con respecto a la formulación del concentrado.

Más particularmente, se ha encontrado que la toxicidad al ojo se puede controlar mediante el control de la concentración molar del ión de amonio del alquilo cuaternario alcoxilado en el concentrado líquido acuoso, incluso concentraciones en peso de la sal de alquilamonio cuaternario alcoxilado que son adecuadas para mejorar sustancialmente la eficiencia herbicida. Esto se puede lograr mediante la selección de un agente tensioactivo de sal de alquilamonio cuaternario alcoxilado que tienen una relación molecular promedio del óxido de alquileo con respecto al amino (W0) en un intervalo intermedio, diluyendo así efectivamente la concentración molar del ión de amonio cuaternario en comparación con un agente tensioactivo que tienen un bajo nivel de W0 en el intervalo de, por decir, 2 a 4. La selección de un agente tensioactivo de sal de amonio cuaternario de dicho valor W0 intermedio logra así una concentración molar relativamente modesta del ión de amonio del alquilo cuaternario alcoxilado que se puede referir como una "dilución intramolecular." En diversas modalidades alternativas, se puede mantener un alto grado de eficiencia herbicida con bajos niveles de toxicidad al ojo mediante la "dilución intermolecular", por ejemplo, mediante la mezcla de una sal de alquilamonio cuaternario alcoxilado con un peso molecular relativamente bajo que tienen un valor W0 en el intervalo entre aproximadamente 2 y aproximadamente 4 con una sal de alquilamonio

cuaternario alcoxlado con un peso molecular relativamente alto que tienen un valor W_0 entre aproximadamente 7 y aproximadamente 15.

Preferiblemente, el sustituyente R en la fórmula anteriormente establecida comprende entre aproximadamente 8 y aproximadamente 18 átomos de carbono, más preferiblemente entre aproximadamente 12 a aproximadamente 18 átomos de carbono. Por lo tanto, un ión de amonio de alquilo cuaternario alcoxlado del valor intermedio W_0 de aproximadamente 5 a aproximadamente 8 típicamente tiene un peso molecular entre aproximadamente 375 y aproximadamente 650 preferiblemente entre aproximadamente 400 y aproximadamente 650. Expresado de otra manera, un agente tensioactivo de cloruro de alquilamonio cuaternario etoxilado de 5 a 8 EO que corresponde a la fórmula anteriormente establecida y derivado a partir de nuez del coco o sebo tiene un contenido N "diluido" entre aproximadamente 0.0015 moles y aproximadamente 0.0025 moles por gramo de agente tensioactivo. Dicha selección de agentes tensioactivos de peso molecular relativamente alto de los valores intermedios W_0 permite que se incorpore un agente tensioactivo de alquilamonio cuaternario alcoxlado a concentraciones en peso relativamente altas dentro de un concentrado acuoso de glifosato de amonio sin exceder las concentraciones molares del agente tensioactivo como se describió anteriormente en la presente invención. Sin atenerse a una teoría particular, se cree que los sustituyentes de alquilo y de óxido de alquilo de peso molecular relativamente alto sirven para reducir la actividad del ión de amonio cuaternario positivamente cargado a una

67
70

concentración dada del mismo, lo cual puede permitir que se utilice una carga de agente tensioactivo ligeramente mayor para una mejor bioeficiencia, sin ocasionar una excesiva irritación al ojo.

Basándose en los mismos intervalos preferidos de los
5 sustituyentes R, una sal de alquilamonio cuaternario alcoxilado de C12 a C18 que tiene un bajo valor W0 entre aproximadamente 2 y aproximadamente 4, típicamente tiene un peso molecular en el intervalo entre aproximadamente 270 y aproximadamente 450, y una sal de alquilamonio cuaternario alcoxilado de C12 a C18 que tiene un valor W0 relativamente alto entre
10 aproximadamente 7 y aproximadamente 15, que tiene un peso molecular en el intervalo entre aproximadamente 490 y aproximadamente 925. Así, por ejemplo, una mezcla que tiene una relación en peso de un 2-4 EO metilcocoamino a 7-15 EO metilcocoamino o metilseboamino entre aproximadamente 1:2 y 2:1 preferiblemente comprende un contenido de N
15 diluido entre aproximadamente 0.0010 y aproximadamente 0.0030, más preferiblemente entre aproximadamente 0.0015 y aproximadamente 0.0025, moles por gramo de agente tensioactivo.

Los ejemplos específicos de las sales mezcladas de alquilamonio cuaternario alcoxilado incluyen mezclas de un cloruro de N-
20 metilcocoamonio etoxilado vendido bajo la designación comercial "Ethaquad C12" que tiene un valor W0 de 2 y un peso molecular de aproximadamente 323 (cuaternario 2 EO ión de N-metilcocoamonio PM = 287; ión cloruro PM = 35.5) y un cloruro de N- metilcocoamonio etoxilado que tiene un valor W0 de

10 y un peso molecular de 539 (cuaternario 10 EO ión de N-metilcocoamonio PM = 503; ión cloruro PM = 35.5) o cloruro de N-metilseboamonio etoxilado que tiene un valor W0 de 10 y un peso molecular de 759 (cuaternario 10 EO ión de N-metilseboamonio PM = 723; ión cloruro PM = 35.5).

- 5 Las formulaciones ejemplares de diamonio que están sustancialmente carentes de cualquier agente tensioactivo no iónico se establecen a continuación:

Formulación A (360 g/L a.e.)

10	glifosato de diamonio	30.3% en peso, a.e.
	N-metilcocoquat 2EO	7.90% a.i.

Formulación B (360 g/L a.e.)

	glifosato de diamonio	30.3% en peso, a.e.
15	N-metiltallowquat 10 EO	2.60% en peso, a.i.
	Metilcocoquat 2EO	2.50% en peso a.i.

Formulación C (360 g/L)

	glifosato de diamonio	30.3% en peso, a.e.
20	N-metilcocoquat 5EO	5.1% en peso, a.i.

formulación D (480 g/L)

	glifosato de diamonio	38.4% en peso, a.e.
	N-metilcocoquat 2EO	7.2% en peso, a.i.

71
72

Formulación E (480 g/L)

glifosato de diamonio	38.4% en peso, a.e.
N-metilcocoquat 2EO	4.62% en peso, a.i.

5

Formulación F (360 g/L a.e.)

glifosato de diamonio	30.3% en peso, a.e.
N-metilcocoquat 2EO	2.00% en peso, a.i.
N-metilcocoquat 1 OEO	3.10% en peso, a.i.
Cantidad de moles de N	0.123

10

Formulación G (360 g/L a.e.)

glifosato de diamonio	30.3% en peso, a.e.
N-metilcocoquat 2EO	2.60% en peso, a.i.
N-metiltallowquat	2.50% en peso, a.i.
Cantidad de moles de N	0.119

15

Formulación H (360 g/L a.e.)

glifosato de diamonio	30.3% en peso, a.e.
N-metiltallowquat 5EO	5.10% en peso, a.i.
Agente tensioactivo no iónico	
Tergitol	1.00% en peso, a.i.
Alcohol lineal C12, 14 (Tergitol)	9 moles de EO

20

Formulación I (480 g/L a.e.)

glifosato de diamonio 38.4% en peso, a.e.

N-metilcocoquat 2EO 4.65% en peso, a.i.

Agente tensioactivo no iónico 1.00% en peso, a.i.

5 OSP Cl 8 Alcohol 9 moles EP 30 moles PO

Todos éstos se llevaron a 100% con agua deionizada. La relación del ión de amonio con respecto a ión de glifosato es de 1.9:1.

De las formulaciones anteriormente establecidas, las formulaciones B, C, F, G y H son de toxicidad excepcionalmente baja al ojo. Estas lograron una clasificación favorable de "amarillo" de conformidad con la prueba de irritación aguda de ojo según la guía OPPTS 870.2400 como se establece por la United States Environmental Protection Agency, EPA712-L-96-195, agosto 1998. Estos resultados contrastan con la clasificación típica de "rojo" para los concentrados con alta carga de glifosato de amonio que contienen sales de alquilamonio cuaternario alcoxilado en la ausencia de concentraciones relativamente altas de agentes tensioactivos no iónicos, o al menos altamente no iónicos a las relaciones de sal de alquilamonio cuaternario alcoxilado.

A continuación la invención se ilustrará por los siguientes ejemplos no limitantes.

EJEMPLOS

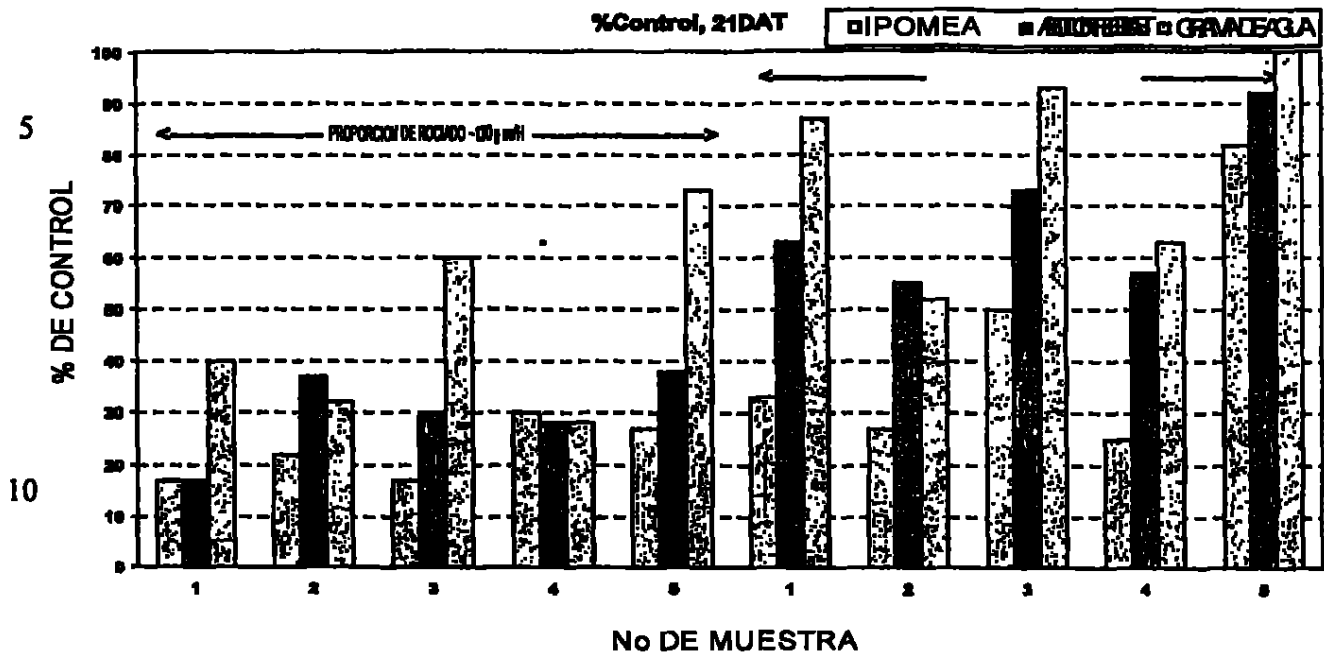
Se llevaron a cabo tres ejemplos por dos agentes de prueba diferentes en tres tiempos diferentes. Se utilizaron tres replicas. La relación de
5 aspersión estuvo en g a.e./H (gramos de glifosato ácido por hectárea). Si la
relación de aspersión era la misma, entonces la concentración del glifosato
era la misma. Todo se asperjaron con soluciones diluidas (a partir de
concentrados) y con el mismo volumen de aspersión. El porcentaje control (%
Control) se comparó en todas las muestras a 21 DAT (días después del
10 tratamiento).

Puesto que es el anión del glifosato el que es biológicamente activo, la concentración de una formulación de glifosato típicamente se expresa como gramos de glifosato ácido por litro (g a.e./l) a 25°C. Debido a esto, la gente compara las formulaciones de glifosato generalmente en el
15 mismo g a.e./l. La concentración de agente tensioactivo típicamente se expresa como gramos de agente tensioactivo activo por litro (g/l). Algunas veces la relación de ácido: agente tensioactivo también se utiliza. Por ejemplo, si una formulación es 540 g a.e./l y el agente tensioactivo es 90 g/l, la relación de ácido: agente tensioactivo es de 6. Por lo tanto, a mayor relación de ácido:
20 agente tensioactivo, menor agente tensioactivo que se encuentra en la formulación.

74
75

EJEMPLO 1

En la figura se muestran cinco ejemplos



Muestra #	Sal de glifosato	Glifosato ácido:agente tensioactivo*	Agente tensioactivo utilizado	Carga de agente tensioactivo* % en peso
1 (Roundup WetherMax)	K	<6	Agente tensioactivo WeatherMax	>7
2 (glifosato de potasio)	K	N.A.	Ninguno	0
3 (catiónicos + no iónicos)	NH ₄	4.3	70% Cocoamida.2EO quat+ 20% dietilenglicol + 10% polietilen (7) alcanol secundario C12-C13	8

25
26

5

4 (cati3nicos + no i3nicos)	NH ₄	9.4	70% Cocoamida.2EO quat + 20% dietilenglicol + 10% polietilen (7) alcanol secundario C12- C13	3.2
5 (cati3nicos)	NH ₄	10.1	75% Cocoamida.2EO quat + 25% dietilenglicol	3

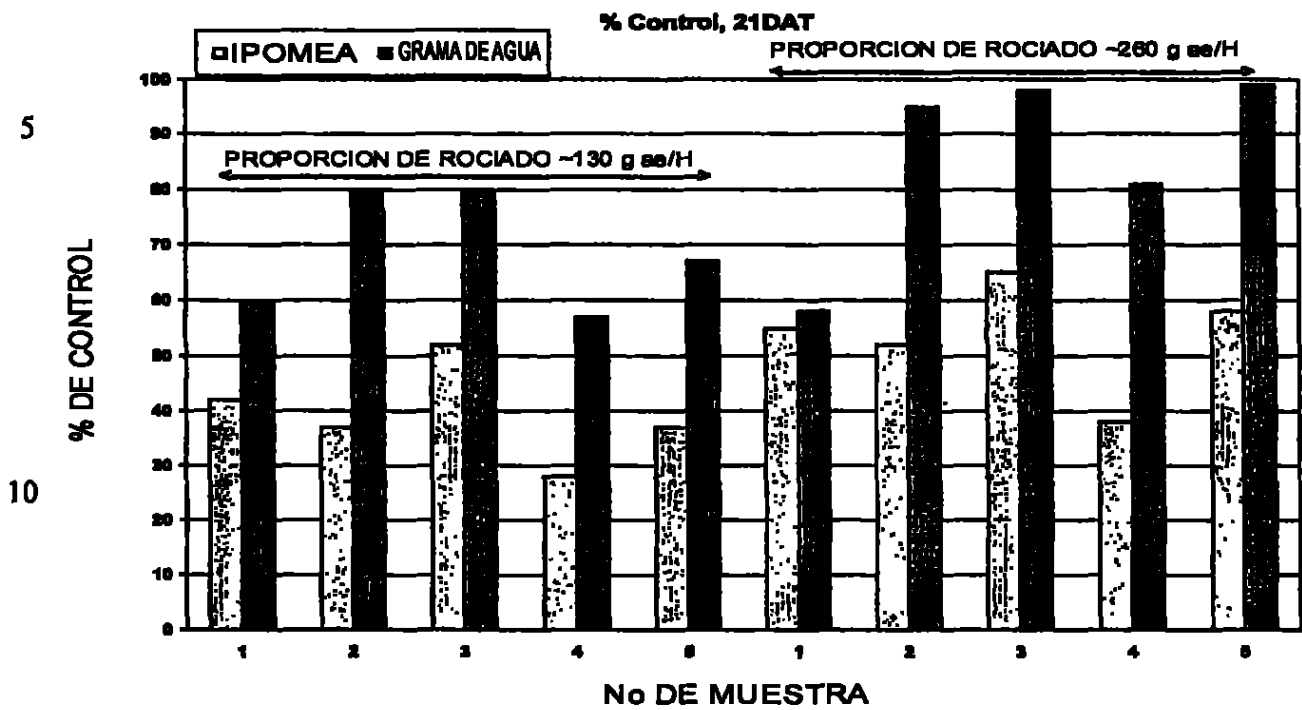
*Esta relaci3n no incluye glicol. Las muestras mostradas en la presente invenci3n son formulaciones lquidas acuosas.

10

Este ejemplo demuestra que el glifosato sin agente tensioactivo (muestra #2) no provee el nivel de control que se observa con dos agentes tensioactivos. En particular, la muestra #5 tuvo una concentraci3n de agente tensioactivo muy baja, mucho menor que los productos comerciales tpicos y menor que la muestra #1, #3, y #4. Sin embargo, la muestra #5 a un tuvo un mayor % Control que las otras muestras. Por el contrario, con el objeto de alcanzar un % Control razonable, el sistema de agente tensioactivo utilizado en la Patente de E.U.A. No. 5998332, en una mezcla de cati3nicos y no i3nicos (muestras #3 y #4), se necesita utilizar a una relaci3n de 3cido: agente tensioactivo de aproximadamente 4.3:1, una concentraci3n m3s de dos veces la concentraci3n en la muestra #5. A la misma concentraci3n de de glifosato, el nivel de control provisto por la muestra #3 fue menor que para la muestra #5 incluso aunque 3sta tuvo una concentraci3n de agente tensioactivo dos veces el nivel encontrado en la muestra #5.

26
77

EJEMPLO 2



En la figura se muestran cinco muestras. Todos fueron sales de

15 glifosato de potasio:

20

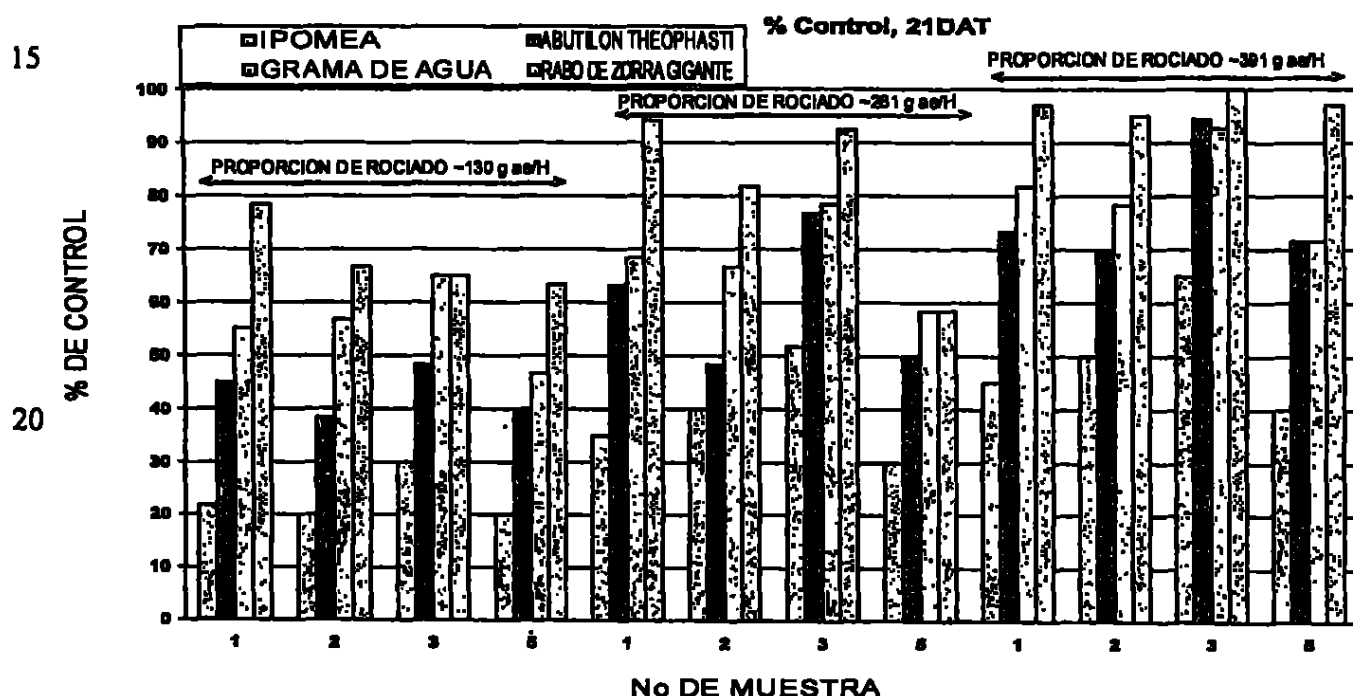
Muestra	Relaci3n de glifosato 3cido/agente tensioactivo*	Agente tensioactivo utilizado	Carga de agente tensioactivo* % en peso
1 (glifosato de potasio)	N.A.	ninguno	0
2 (WeatherMax)	<6	Agente tensioactivo WeatherMax	>7
3 (cati3nicos)	7.51	75% cocoamina-2EO quat + 25% propilenglicol	4
4 (etoxilato de amina)	6.12	Tallowamina-10EO	6.5
5 (etoxilato de eteramina)	4.4	Polioxietilen (5) alcohol lineal C12-C14 (oxipropil) ₂ amina	9

*Esta relación no incluye glicol. Las muestras mostradas en la presente invención son formulaciones líquidas acuosas.

En este ejemplo, la muestra #3 tuvo una concentración muy baja de agente tensioactivo, mucho menor que los productos comerciales típicos y menor que las muestras #2, #4 y #5. Sin embargo, la muestra #3 a un tuvo un % control mayor o equivalente que las otras muestras. A la misma concentración de glifosato, la muestra #3 tuvo un control equivalente al de la muestra #5 en % Control aún cuando ésta tuvo una concentración de agente tensioactivo dos veces menor en comparación con la muestra #5.

Además, solamente la muestra #3 fue estable entre -20 y 60°C a una concentración de más de 540 g a.e./l.

EJEMPLO 3



Las muestras que se muestran en la figura fueron las mismas que aquéllas en el ejemplo 2 (la muestra #4 no se utilizó aquí). De nuevo, en este ejemplo, la muestra #3 fue equivalente a o mejor que las otras muestras en el % Control.

Como se muestra en los ejemplos anteriores, sea descubierto de manera inesperada que un agente tensioactivo altamente efectivo y eficiente, de alquilamina cuaternarios alcoxilada, pueden mejorar significativamente la eficiencia de una formulación de glifosato. Además, el agente tensioactivo de alquilamina alcoxilada cuaternaria es estable en todas las sales de las formulaciones de glifosato (incluyendo potasio y amonio) incluso a una concentración muy elevada (470 - 600 g a.e./l). Se espera que este resultado provea ahorros significativos en los costos de las materias primas para las formulaciones de glifosato y mejorarán las logísticas del manejo de agentes tensioactivos en las plantas.

NOVEDAD DE LA INVENCION

REIVINDICACIONES

5 1.- Una formulación herbicida, estable que comprende al menos un compuesto herbicidamente activo y un agente tensioactivo adyuvante, en donde dicho agente tensioactivo adyuvante comprende al menos un agente tensioactivo catiónico de amonio cuaternario alcoxilado.

10 2.- La formulación de conformidad con la reivindicación 1, caracterizada además porque dicha formulación sustancialmente no contiene polioxietileno alquiléteres.

3.- La formulación de conformidad con la reivindicación 2, caracterizada además porque dicha formulación contiene menos de aproximadamente 0.2% en peso de otros agentes tensioactivos.

15 4.- La formulación de conformidad con la reivindicación 3, caracterizada además porque dicha formulación contiene menos de aproximadamente 0.1% en peso de otros agentes tensioactivos.

20 5.- La formulación de conformidad con la reivindicación 4, caracterizada además porque dicha formulación no contiene cantidades sustanciales de otros agentes tensioactivos.

6.- La formulación de conformidad con la reivindicación 1, caracterizada además porque dicho compuesto herbicidamente activo es una sal de glifosato.

7.- La formulación de conformidad con la reivindicación 1, caracterizada además porque dicha formulación es estable entre -20 y 60°C, preferiblemente -10 a 50°C y más preferiblemente 0 y 40°C.

8.- La formulación de conformidad con la reivindicación 1,
5 caracterizada adicionalmente porque comprende al menos un auxiliar de procesamiento.

9.- La formulación de conformidad con la reivindicación 8, caracterizada además porque dicho auxiliar de procesamiento es un glicol.

10.- La formulación de conformidad con la reivindicación 1,
10 caracterizada además porque dicho compuesto cuaternario alcoxilado es cloruro de metil bis(2-hidroxietil)coco amonio.

11.- La formulación de conformidad con la reivindicación 6, caracterizada además porque la sal de glifosato se selecciona a partir del grupo de sodio, potasio, amonio, isopropilamina, monoetanolamina,
15 dietanolamina, trietanolamina, trimetilsulfonio, y mezclas de los mismos.

12.- La formulación de conformidad con la reivindicación 11, caracterizada además porque la formulación de glifosato es una formulación líquida estable con una concentración de glifosato en el intervalo de 360-600 g a.e./l, preferiblemente 450-580 a.e./l.

20 13.- La formulación de conformidad con la reivindicación 6, caracterizada además porque la relación de glifosato (% en peso a.e.) con respecto al compuesto de amonio cuaternario alcoxilado es entre 4:1 y 100:1.

14.- La formulación de conformidad con la reivindicación 13, caracterizada además porque la relación de glifosato (% en peso a.e.) con respecto al compuesto de amonio cuaternario alcoxlado es entre 7:1 y 40:1.

5 15.- La formulación de conformidad con la reivindicación 14, caracterizada además porque la relación de glifosato (% en peso a.e.) cCon respecto al compuesto de amonio cuaternario alcoxlado es entre 10:1 y 30:1.

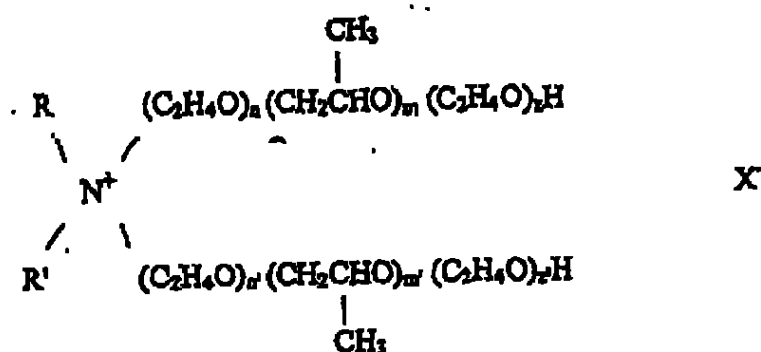
16.- La formulación de conformidad con la reivindicación 1, caracterizada además porque la cual comprende adicionalmente un co-herbicida.

10 17.- La formulación de conformidad con la reivindicación 16, caracterizada además porque dicho co-herbicida se selecciona a partir del grupo que consiste esencialmente de sulfonilurea, acifluorfen, asulam, benzolina, bentazon, bialafos, bromacil, bromoxinil, cloramben, clopiralid, 2,4-D, 2,4-DB, dalapon, dicamba, diclorprop, diclofop, diquat, endotall, fenac, 15 fenoxaprop, flamprop, fluazifop, fluoroglicofén, fomesafen, fosamina, glufosinato, haloxifop, imazamet, imazametabenz, imazamox, imazapir, imazaquin, imazetapir, ioxinil, MCPA, MCPB, mecoprop, ácido metilarsónico, naptalam, ácido nonanóico, paraquat, picloram, ácido sulfámico, 2,3,6-TBA, TCA, triclopir, sales de los mismos, y mezclas de los mismos.

20 18.- La formulación de conformidad con la reivindicación 1, caracterizada además porque dicho compuesto de amonio cuaternario alcoxlado es de la fórmula general I, a continuación:

87
83

5



en donde R es un grupo alquileo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquileo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, y $n+n'$ es un entero de 0-30, $m + m'$ es un entero de 0 a 30, y $z + z'$ es un entero de 0-30, con la condición de que $n + z$ es al menos 1 y/o $n' + z'$ es al menos 0 ó 1, y X^- es un anión compatible en agricultura.

19.- La formulación de conformidad con la reivindicación 18, caracterizada además porque dicho compuesto de amonio cuaternario alcoxilado es cloruro de metil bis(2-hidroxietil)coco amonio.

20.- La formulación de conformidad con la reivindicación 19, caracterizada además porque dicha formulación es un sólido.

21.- la formulación de conformidad con la reivindicación 20, caracterizada además porque dicha formulación comprende al menos un agente tensioactivo cuaternario alcoxilado y una sal de glifosato, en donde la relación de agente tensioactivo: sal es entre 4:1 y 100:1.

22.- La formulación de conformidad con la reivindicación 1, caracterizada además porque dicho al menos un compuesto herbicida

activo se selecciona a partir del grupo que consiste esencialmente de sulfonilurea, acifluorfen, asulam, benzolina, bentazon, bialafos, bromacil, bromoxinil, cloramben, clopiralid, 2,4-D, 2,4-DB, dalapon, dicamba, diclorprop, diclofop, diquat, endotall, fenac, fenoxaprop, flamprop, fluazifop, fluoroglicofén, fomesafen, fosamina, glufosinato, haloxifop, imazamet, imazametabenz, imazamox, imazapir, imazaquin, imazetapir, ioxinil, MCPA, MCPB, mecoprop, ácido metilarsónico, naptalam, ácido nonanóico, paraquat, picloram, ácido sulfámico, 2,3,6-TBA, TCA, triclopir, sales de los mismos, y mezclas de los mismos.

23.- Un concentrado herbicida líquido acuoso estable que comprende una sal de amonio de glifosato y que contiene al menos aproximadamente 240 gramos/L de glifosato a.e., ión de amonio en una relación molar con respecto al glifosato entre aproximadamente 0.8 y aproximadamente 2.5, y al menos un agente tensioactivo de sal de alquilamonio cuaternario alcoxilado que corresponde a la fórmula:



en donde R es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, A es $(R^2O)p(R^3O)q(R^4O)zR^8$ y B es $(R^5O)p'(R^6O)q'(R^7O)z'R^9$ en donde cada uno de R^2 , R^3 , R^4 , R^5 , R^6 , y R^7 se selecciona independientemente a partir del grupo que consiste de etileno e isopropileno, cada uno de R^8 y R^9 se selecciona a partir del grupo que

consiste de hidrógeno, metilo y etilo, y cada uno de p , q , p' , q' , z y z' es independientemente un entero entre 0 y 30 y la suma de $p + p' + q + q' + z + z'$ es al menos aproximadamente 2, la relación en peso de la suma de todos los agentes tensioactivos de sal de amonio cuaternario del alquilo alcoxilado con respecto al alquil éter de óxido de polialquileno siendo mayor de 4.5:1.

24.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxilado con respecto a la suma de dichos agentes tensioactivos no iónicos siendo mayor de 4.5:1.

25.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxilado con respecto a la suma de cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileno siendo mayor de 5.2:1.

26.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 25, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxilado con respecto a la suma de cualesquiera agentes tensioactivos no iónicos siendo mayor de 5.2:1.

27.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 25, caracterizado además porque la relación

86

en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileo siendo mayor de 10:1.

5 28.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera agentes tensioactivos no iónicos siendo mayor de 10:1.

10 29.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque comprende al menos aproximadamente 325 g/L de glifosato, a.e.

 30.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 29, caracterizado además porque
15 comprende al menos aproximadamente 380 g/L de glifosato, a.e.

 31.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 30, caracterizado además porque comprende al menos aproximadamente 400 g/L de glifosato, a.e.

 32.- El concentrado herbicida líquido acuoso estable de
20 conformidad con la reivindicación 23, caracterizado además porque no contiene más de aproximadamente 5% en peso de sulfato de amonio.

 33.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la relación

26
87

de la suma de agentes tensioactivos de la sal de alquilamonio cuaternario dialcoxilado con respecto a la suma de (alquilen glicol(es) + alquilen éter glicol(es)) es mayor de aproximadamente 3.25.

34.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la relación de la suma de agentes tensioactivos de la sal de alquilamonio cuaternario dialcoxilado con respecto a la suma de (alquilen glicol(es) + alquilen éter glicol(es)) es mayor de aproximadamente 4.

35.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque $(p+q+p'+q'+z+z') \geq 3$.

36.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque dichos agentes tensioactivos de alquilamina cuaternaria alcoxilada tienen un valor W_0 entre aproximadamente 3 y aproximadamente 20, en donde W_0 es el valor promedio de $(p + p' + q + q' + z + z')$ para dichos agentes tensioactivos.

37.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 36, caracterizado además porque el valor W_0 es entre aproximadamente 3 y aproximadamente 7.

38.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 36, caracterizado además porque el valor W_0 es entre aproximadamente 6 y aproximadamente 15.

39.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 36, caracterizado además porque comprende una pluralidad de agentes tensioactivos de alquilamonio cuaternario alcoxilado, el valor de W_0 para al menos uno de dicha pluralidad de agentes tensioactivos siendo entre aproximadamente 2, y el valor de X_0 para el otro de dichos agentes tensioactivos estando en el intervalo de entre aproximadamente 8 y aproximadamente 15.

40.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 39, caracterizado además porque R de al menos uno de dicha pluralidad de agentes tensioactivos de sal de alquilamina cuaternaria alcoxilada contiene un promedio de entre aproximadamente 16 y aproximadamente 18 átomos de carbono.

41.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque R de al menos uno de dicha pluralidad de agentes tensioactivos de sal de alquilamonio cuaternario alcoxilado contiene un promedio de entre aproximadamente 16 y aproximadamente 18 átomos de carbono.

42.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 41, caracterizado además porque R de dicho agente tensioactivo de alquilamina cuaternaria alcoxilada se deriva predominantemente a partir de sebo.

43.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la relación

molar de iones de amonio con respecto a los iones de glifosato es de al menos aproximadamente 1.1.

44.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la relación
5 molar de iones de amonio con respecto a los iones de glifosato es de al menos aproximadamente 1.5.

45.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la relación en peso de glifosato, a.e., con respecto a la suma de sales de alquilamonio
10 cuaternario alcoxilado se encuentra entre aproximadamente 3 y aproximadamente 20.

46.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 45, caracterizado además porque la relación en peso de glifosato, a.e., con respecto a la suma de sales de alquilamonio
15 cuaternario alcoxilado se encuentra entre aproximadamente 3 y aproximadamente 10.

47.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 23, caracterizado además porque la concentración de la suma de agentes tensioactivos de la sal de alquilamonio
20 cuaternario alcoxilado se encuentra entre aproximadamente 3% en peso y aproximadamente 12% en peso.

48.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 47, caracterizado además porque la

concentración de la suma de agentes tensioactivos de la sal de alquilamonio cuaternario alcoxlado se encuentra entre aproximadamente 3.5% en peso y aproximadamente 10% en peso.

49.- El concentrado herbicida líquido acuoso estable de
5 conformidad con la reivindicación 23, caracterizado además porque tiene una baja toxicidad al ojo.

50.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 49, caracterizado además porque tiene una clasificación de amarilla en la toxicidad al ojo en banda roja.

10 51.- El concentrado herbicida líquido acuoso estable que comprende una sal de amonio del glifosato y que contiene al menos aproximadamente 240 g/L de glifosato a.e., ion de amonio en una relación molar con respecto al glifosato entre aproximadamente 0.8 y aproximadamente 2.5, y al menos un agente tensioactivo de sal del
15 alquilamonio cuaternario alcoxlado predominantemente que comprende un sustituyente N-alquilo derivado a partir de sebo.

52.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 51, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de
20 alquilamonio cuaternario alcoxlado con respecto la suma de cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileo es mayor de 4.5:1.

53.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 51, caracterizado además porque comprende al menos aproximadamente 325 gpl de glifosato, a.e.

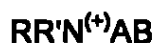
54.- El concentrado herbicida líquido acuoso estable de
5 conformidad con la reivindicación 23, caracterizado además porque comprende una sal de amonio del glifosato y contiene más de 38.0% en peso/L de glifosato a.e., ión de amonio en una relación molar con respecto al glifosato entre aproximadamente 0.8 y aproximadamente 2.5, al menos un agente tensioactivo de sal de alquilamonio cuaternario alcoxlado en donde
10 cada uno de p, q, p' y q' es independientemente un entero entre 0 y 3, dicho concentrado teniendo un pH < 7.3.

55.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 54, caracterizado además porque la relación en peso de la suma de los agentes tensioactivos de sal de alquilamonio cuaternarios alcoxlado con respecto a cualquier agentes tensioactivo de alquil éter de óxido de polialquilenos es mayor de 4:1.
15

56.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 54, caracterizado además porque dicho concentrado tiene una concentración de amoniaco en la solución que es
20 menor de aproximadamente 750 ppm a 25°C.

57.- Un concentrado herbicida líquido acuoso estable que comprende un sal de amonio del glifosato y que contiene al menos aproximadamente 120 g/L de glifosato a.e., ión de amonio en una relación

molar al glifosato entre aproximadamente 0.75 y aproximadamente 2.5, y al menos un agente tensioactivo de sal de alquilamonio cuaternario alcoxilado que corresponde a la fórmula:



- 5 en donde R es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, A es $(R^2O)p(R^3O)q(R^4O)zR^6$ y B es $(R^5O)p'(R^6O)q'(R^7O)z'R^9$ en donde cada uno de R^2 , R^3 , R^4 , R^5 , R^6 , y R^7 se
- 10 selecciona independientemente a partir del grupo que consiste de etileno e isopropileno, y cada uno de p, q, p', q', z y z' es independientemente un entero entre 0 y 30 y la suma de $[p + p' + q + q' + z + z']$ es al menos aproximadamente 2, la relación en peso del total de agentes tensioactivos de alquilamonio cuaternario alcoxilado con respecto al glifosato de amonio, a.e.,
- 15 en dicho concentrado estando entre aproximadamente 0.1:1 y aproximadamente 0.2:1, y la concentración molar del ión de alquilamonio cuaternario alcoxilado en dicha concentración acuosa no siendo mayor de aproximadamente 0.28.

- 58.- El concentrado líquido acuoso estable de conformidad con
- 20 la reivindicación 57, caracterizado además por que la relación molar de dicho agente tensioactivo de sal de alquilamonio cuaternario alcoxilado no es mayor de aproximadamente 0.25, 0.20, 0.15, 0.13, 0.10 ó 0.08.
-

59.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque R comprende entre aproximadamente 8 y aproximadamente 18 átomos de carbono

5 60.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 59, caracterizado además porque R se deriva predominantemente partir de cebo.

61.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque la relación
10 en peso de la suma de todos esos agentes tensioactivos de sal de amonio cuaternario alquilo alcoxlado con respecto a cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileno, siendo mayor de 4.5:1.

62.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 61, caracterizado además porque la relación
15 en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera agentes tensioactivos no iónicos siendo mayor de 4.5:1.

63.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque la relación
20 en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileno siendo mayor de 5.2:1.

64.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 63, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera
5 agentes tensioactivos no iónicos siendo mayor de 5.2:1.

65.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 63, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera
10 agentes tensioactivos de alquil éter de óxido de polialquileo siendo mayor de 10:1.

66.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 65, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de sal de
15 alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera agentes tensioactivos no iónicos siendo mayor de 10:1.

67.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque comprende al menos aproximadamente 240 gpl de glifosato, a.e.

20 68.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque comprende al menos aproximadamente 325 gpl de glifosato, a.e.

69.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 68, caracterizado además porque comprende al menos aproximadamente 360 g/L de glifosato, a.e.

5 70.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 69, caracterizado además porque comprende al menos aproximadamente 400 g/L de glifosato, a.e.

71.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque no contiene más de aproximadamente 5% en peso de sulfato de amonio.

10 72.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque la relación de la suma de agentes tensioactivos de la sal de alquilamonio cuaternario dialcoxilado con respecto a la suma de (alquilen glicol(es) + alquilen éter glicol(es)) es mayor de aproximadamente 3.25.

15 73.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque la relación de la suma de agentes tensioactivos de la sal de alquilamonio cuaternario dialcoxilado con respecto a la suma de (alquilen glicol(es) + alquilen éter glicol(es)) es mayor de aproximadamente 4.

20 74.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque tiene una clasificación de amarilla en la toxicidad al ojo en banda roja.

95
96

75.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque la concentración molar de ión de alquilamonio cuaternario alcoxilado no es mayor de aproximadamente 0.13.

5 76.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque la concentración molar de todos los iones de amonio cuaternario no es mayor de aproximadamente 0.15.

77.- un concentrado herbicida líquido acuoso estable que
10 comprende una sal de amonio de glifosato y que contiene al menos aproximadamente 120 gramos/L de glifosato a.e., ión de amonio en una relación molar con respecto al glifosato entre aproximadamente 0.75 y aproximadamente 2.5, y al menos un agente tensioactivo de sal de alquilamonio cuaternario alcoxilado que corresponde a la fórmula:

15
$$RR'N^{(+)}AB$$

en donde R es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, A es $(R^2O)p(R^3O)q(R^4O)zR^8$ y B es
20 $(R^5O)p'(R^6O)q'(R^7O)z'R^9$ en donde cada uno de R^2 , R^3 , R^4 , R^5 , R^6 , y R^7 se selecciona independientemente a partir del grupo que consiste de etileno e isopropileno, y cada uno de p, q, p', q', z y z' es independientemente un entero entre 0 y 30 y la suma de $[p + p' + q + q' + z + z']$ es al menos

aproximadamente 2, la relación en peso del total de agentes tensioactivos de alquilamonio cuaternario alcoxlado con respecto al glifosato de amonio, a.e., en dicha concentración estando entre aproximadamente 0.1:1 y aproximadamente 0.2:1, y el valor promedio de $(p+p'+q+q'+z+z')$ para dicho al menos un agente tensioactivo es entre aproximadamente 2 y aproximadamente 10.

78.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 57, caracterizado además porque el valor promedio de $(p+p'+q+q'+z+z')$ para dicho al menos un agente tensioactivo es entre aproximadamente 3 y aproximadamente 10, o entre aproximadamente 3 y aproximadamente 8 o entre aproximadamente 4 y aproximadamente 8 o entre aproximadamente 5 y aproximadamente 10.

79.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 77, caracterizado además porque la concentración molar del ión de alquilamonio cuaternario alcoxlado no es mayor de aproximadamente 0.28.

80.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 77, caracterizado además porque la concentración molar total de todos los iones de amonio cuaternario no es mayor de aproximadamente 0.15.

81.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 77, caracterizado además porque comprende al menos dos agentes tensioactivos de sal de alquilamonio

cuaternario alcoxlado, en donde la suma promedio de $(p+p'+q+q'+z+z')$ para uno de dichos al menos dos agentes tensioactivos siendo entre aproximadamente 2 y aproximadamente cinco, y la suma promedio de $(p+p'+q+q'+z+z')$ para otro de dichos al menos dos agentes tensioactivos
5 siendo entre aproximadamente 5 y aproximadamente 15.

82.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 81, caracterizado además porque la relación en peso de la suma de dicho uno y dicho otro agentes tensioactivos con respecto al glifosato de amonio, a.e., siendo entre aproximadamente 0.1:1 y 0.2:1.

10 83.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 82, caracterizado además porque la relación en peso de dicho un agente tensioactivo con dicho otro agente tensioactivo es entre aproximadamente 1:1.5 y aproximadamente 1.5:1.

- 15 84.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 81, caracterizado además porque la relación molar de los agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto al glifosato no es mayor de aproximadamente 0.2:1.

20 85.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 81, caracterizado además porque la relación entre peso de los agentes tensioactivos de sal de alquilamonio cuaternario alcoxlado con respecto al glifosato se encuentra entre aproximadamente 0.1:1 y aproximadamente 0.17:1.

86.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 81, caracterizado además porque la concentración molar del ión de alquilamonio cuaternario alcoxilado en dicho concentrado acuoso no es mayor de aproximadamente 0.15.

5 87.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 81, caracterizado además porque la concentración molar total de todos los iones de amonio cuaternario no es mayor aproximadamente 0.15.

10

MA

15 P07/520F(reivindicaciones)

RESUMEN DE LA INVENCION

La presente invención se refiere a formulaciones estables de
glifosato con eficiencia mejorada por un agente tensioactivo cuaternario de
5 alquilamonio alcoxilado altamente efectivo a un nivel utilizado muy bajo; el
agente tensioactivo cuaternario de alquilamina alcoxilada es compatible en
todas las formulaciones de sales de glifosato (incluyendo potasio y amonio)
incluso a una concentración muy elevada (470 - 600 g a.e./l).

10

15

20 MA
P07/520F

**AMENDED
CLAIMS**

102

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

1

1. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 240 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.8 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ and B is $(R^5O)_p'(R^6O)_q'(R^7O)_z'R^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, each of R^8 and R^9 is selected from the group consisting of hydrogen, methyl and ethyl, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $p + p' + q + q' + z + z'$ is at least about 2,

the weight ratio of the sum of all said alkoxyated alkyl quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) being greater than 4.5:1. [Article 34 Amendment claim 15]

2. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 4.5:1.

3. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 5.2:1.

4. A stable aqueous liquid herbicidal concentrate as set forth in claim 3 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 5.2:1.

103

5. A stable aqueous liquid herbicidal concentrate as set forth in claim 3 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 10:1.

6. A stable aqueous liquid herbicidal concentrate as set forth in claim 5 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 10:1.

7. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 comprising at least about 325 gpl glyphosate, a.e.

8. A stable aqueous liquid herbicidal concentrate as set forth in claim 7 comprising at least about 360 g/L glyphosate, a.e.

9. A stable aqueous liquid herbicidal concentrate as set forth in claim 8 comprising at least about 400 g/L glyphosate, a.e.

10. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 containing not more than about 5 wt.% ammonium sulfate.

11. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 3.25.

12. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 4.

103
104

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

3

13. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein $(p + q + p' + q' + z + z') \geq 3$.

14. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein said alkoxyated quaternary alkylamine surfactant(s) have a W_0 value between about 3 and about 20, where W_0 is the average value of $(p + p' + q + q' + z + z')$ for said surfactant(s).

15. A stable aqueous liquid herbicidal concentrate as set forth in claim 14 comprising a plurality of alkoxyated quaternary alkylammonium surfactants, the value of W_0 for at least one of said plurality of surfactants being about 2, and the value of W_0 for the other of said surfactants being in the range of between about 8 and about 15.

16. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein R of at least one of said plurality of alkoxyated quaternary alkylamine salt surfactants contains an average between about 16 and about 18 carbon atoms.

17. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein R of said alkoxyated quaternary alkylammonium salt surfactant(s) contains an average of between about 16 and about 18 carbon atoms.

18. A stable aqueous liquid herbicidal concentrate as set forth in claim 17 wherein R of said alkoxyated quaternary alkylamine salt surfactant is derived predominantly from tallow.

19. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the molar ratio of ammonium ions to glyphosate ions is at least about 1.2.

20. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the weight ratio of glyphosate, a.e., to the sum of alkoxyated quaternary alkylammonium salt(s) is between about 3 and about 20.

21. A stable aqueous liquid herbicidal concentrate as set forth in claim 20 wherein the weight ratio of glyphosate, a.e., to the sum of alkoxyated quaternary alkylammonium salt(s) is between about 3 and about 10.

105

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

4

22. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the concentration of the sum of alkoxyated quaternary alkylammonium salt surfactant(s) is between about 3 wt.% and about 12 wt.%.

23. A stable aqueous liquid herbicidal concentrate as set forth in claim 22 wherein the concentration of the sum of alkoxyated quaternary alkylammonium salt surfactant(s) is between about 3.5 wt.% to about 10 wt.%.

24. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 having a Red Band eye toxicity classification of yellow.

25. The stable aqueous liquid herbicidal concentrate of claim 1 comprising an ammonium salt of glyphosate and containing greater than 38.0 wt.% /L glyphosate a.e., at least one alkoxyated quaternary alkylammonium salt surfactant wherein each of p, q, p' and q' is independently an integer between 0 and 3, said concentrate having a pH <7.3.

26. The stable aqueous liquid herbicidal concentrate of claim 25, said concentrate having an ammonia concentration over the solution that is less than about 750 ppm at 25°C.

27. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and the molar concentration of alkoxyated quaternary alkylammonium ion in said aqueous concentrate being not greater than about 0.28.

28. A stable aqueous liquid concentrate as set forth in claim 27 wherein the molar concentration of said alkoxyated quaternary alkylammonium salt surfactant is not greater than about 0.15.

29. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 wherein R comprises between about 8 and about 18 carbon atoms.

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

5

30. A stable aqueous liquid herbicidal concentrate as set forth in claim 29 wherein R is predominantly derived from tallow.

31. A stable aqueous liquid herbicidal concentrate as set forth in claim 28 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 4.5:1.

32. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 5.2:1.

33. A stable aqueous liquid herbicidal concentrate as set forth in claim 32 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 5.2:1.

34. A stable aqueous liquid herbicidal concentrate as set forth in claim 32 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 10:1.

35. A stable aqueous liquid herbicidal concentrate as set forth in claim 34 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 10:1.

36. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 comprising at least about 325 gpl glyphosate, a.e.

37. A stable aqueous liquid herbicidal concentrate as set forth in claim 36 comprising at least about 360 g/L glyphosate, a.e.

105
107

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

6

38. A stable aqueous liquid herbicidal concentrate as set forth in claim 37 comprising at least about 400 g/L glyphosate, a.e.

39. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 containing not more than about 5 wt.% ammonium sulfate.

40. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 wherein the ratio of the sum of dialkoxylated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 3.25.

41. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 wherein the ratio of the sum of dialkoxylated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 4.

42. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 having a Red Band eye toxicity classification of yellow.

43. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 wherein the molar concentration of alkoxylated quaternary alkylammonium ion is not greater than about 0.13.

44. A stable aqueous liquid herbicidal concentrate as set forth in claim 27 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

45. A stable aqueous liquid herbicidal concentrate as set forth in claim 1 wherein the weight ratio of the total of alkoxylated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and the number average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 2 and about 10.

107

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

7

46. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 120 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.75 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ and B is $(R^5O)_p'(R^6O)_q'(R^7O)_z'R^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $[p + p' + q + q' + z + z']$ is at least about 2, the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 3 and about 10. [Article 34 Amendment claim 77]

47. An aqueous liquid herbicidal concentrate as set forth in claim 46 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 3 and about 8.

48. An aqueous liquid herbicidal concentrate as set forth in claim 46 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 4 and about 8.

49. An aqueous liquid herbicidal concentrate as set forth in claim 46 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 5 and 10.

50. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 120 g/L glyphosate a.e., ammonium ion in a molar ratio

109

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

8

to glyphosate between about 0.75 and about 2.5, and at least two alkoxyated quaternary alkylammonium salt surfactants corresponding to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ and B is $(R^5O)_p(R^6O)_q(R^7O)_zR^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $[p + p' + q + q' + z + z']$ is at least about 2,

the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and

the average sum of $(p + p' + q + q' + z + z')$ for one of said at least two surfactants being between about 2 and about 5, and the average sum of $(p + p' + q + q' + z + z')$ for another of said at least two surfactants being between about 5 and about 15. [Article 34 Amendment claim 81]

51. An aqueous liquid herbicidal concentrate as set forth in claim 50 wherein the weight ratio of the sum of said one and said another surfactants to ammonium glyphosate, a.e., being between about 0.1:1 and about 0.2:1.

52. An aqueous liquid herbicidal concentrate as set forth in claim 51 wherein the weight ratio of said one surfactant to said another surfactant is between about 1:1.5 and about 1.5:1.

53. An aqueous liquid herbicidal concentrate as set forth in claim 50 wherein the mole ratio of alkoxyated quaternary alkylammonium salt surfactant(s) to glyphosate is not greater than about 0.2:1.

120
710

PCT/US2005/034076
NATIONAL STAGE CLAIMS
(ACA6355WO; 39-21(54049); MTC 6920.8)

9

54. An aqueous liquid herbicidal concentrate as set forth in claim 50 wherein the weight ratio of alkoxylated quaternary alkylammonium salt surfactant(s) to glyphosate is between about 0.1:1 and about 0.17:1.

55. An aqueous liquid herbicidal concentrate as set forth in claim 50 wherein the molar concentration of alkoxylated quaternary alkylammonium ion in said aqueous concentrate is not greater than about 0.15.

56. An aqueous liquid herbicidal concentrate as set forth in claim 50 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

57. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 240 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.8 and about 2.5, and at least one alkoxylated quaternary alkylammonium salt surfactant predominantly comprising an N-alkyl substituent derived from tallow. [Article 34 Amendment claim 43.]

58. A stable aqueous liquid concentrate as set forth in claim 57 wherein the weight ratio of the sum of all said alkoxylated alkyl quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) is greater than 4.5:1.

59. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 comprising at least about 325 gpl glyphosate, a.e.

~~140~~
141

REIVINDICACIONES MODIFICADAS

NUEVEDAD DE LA INVENCION**REIVINDICACIONES**

- 5 1.- Un concentrado herbicida líquido acuoso estable que comprende un sal de amonio del glifosato y que contiene al menos aproximadamente 240 g/L de glifosato a.e., ión de amonio en una relación molar de glifosato entre aproximadamente 0.8 y aproximadamente 2.5, y al menos un agente tensioactivo de sal de alquilamonio cuaternario alcoxilado
- 10 que corresponde a la fórmula: $RR'N^{(+) }AB$; en donde R es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, A es $(R^2O)p(R^3O)q(R^4O)zR^6$ y B es $(R^5O)p'(R^6O)q'(R^7O)z'R^9$ en donde cada uno de
- 15 R^2 , R^3 , R^4 , R^5 , R^6 , y R^7 se selecciona independientemente a partir del grupo que consiste de etileno e isopropileno, cada uno de R^8 y R^9 se selecciona a partir del grupo que consiste de hidrógeno, metilo y etilo, y cada uno de p, q, p', q', z y z' es independientemente un entero entre 0 y 30 y la suma de $p + p' + q + q' + z + z'$ es al menos aproximadamente 2, la relación en peso de la
- 20 suma de todos esos agentes tensioactivos de la sal de amonio cuaternario del alquilo alcoxilado con respecto a cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileno es mayor de 4.5:1.
-

2.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxlado con respecto la suma de cualesquiera
5 agentes tensioactivos no iónicos es mayor de 4.5:1.

3.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera
10 agentes tensioactivos de alquil éter de óxido de polialquileo es mayor de 5.2:1.

4.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 3, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxlado con respecto la suma de cualesquiera
15 agentes tensioactivos no iónicos es mayor de 5.2:1.

5.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 3, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxlado con respecto a la suma de cualesquiera
20 agentes tensioactivos de alquil éter de óxido de polialquileo es mayor de 10:1.

6.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 5, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxilado con respecto la suma de cualesquiera 5 agentes tensioactivos no iónicos es mayor de 10:1.

7.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque comprende al menos aproximadamente 325 gpl de glifosato, a.e.

8.- El concentrado herbicida líquido acuoso estable de 10 conformidad con la reivindicación 7, caracterizado además porque comprende al menos aproximadamente 360 g/L de glifosato, a.e.

9.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 8, caracterizado además porque comprende al menos aproximadamente 400 g/L de glifosato, a.e.

15 10.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque contiene no más de aproximadamente 5% en peso de sulfato de amonio.

11.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación 20 de la suma de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario dialcoxilado con respecto a la suma de (alquilen glicol(es) + Alquilen éter glicol(es)) es mayor de aproximadamente 3.25.

12.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación de la suma de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario dialcoxilado con respecto a la suma de (alquilen glicol(es) + alquilen éter glicol(es)) es mayor de aproximadamente 4.

13. El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque $(p + q + p' + q' + z + z') \geq 3$.

14.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque dicho agente tensioactivo(s) de alquilamina cuaternaria alcoxilada tiene un valor W_0 entre aproximadamente 3 y aproximadamente 20, en donde W_0 es el valor promedio de $(p + p' + q + q' + z + z')$ para dicho agente(s) tensioactivo(s).

15.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 14, caracterizado además porque comprende una pluralidad de agentes tensioactivos de alquilamonio cuaternario alcoxilado, el valor de W_0 para al menos uno de dicha pluralidad de agentes tensioactivos siendo de aproximadamente 2, y el valor de W_0 para el otro de dichos agentes tensioactivos estando en el intervalo de entre aproximadamente 8 y aproximadamente 15.

16.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 15, caracterizado además porque R de al menos uno de dicha pluralidad de agentes tensioactivos de sal de alquilamina

126

cuaternaria alcoxilada que contiene un promedio de entre aproximadamente 16 y aproximadamente 18 átomos de carbono.

17.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque R de dicho(s) agente(s) tensioactivo(s) de sal de alquilamonio cuaternario alcoxilado contiene un promedio de entre aproximadamente 16 y aproximadamente 18 átomos de carbono.

18.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 17, caracterizado además porque R de dicho agente tensioactivo de sal de alquilamina cuaternaria alcoxilada se deriva predominantemente a partir de sebo.

19.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación molar de los iones de amonio con respecto a los iones de glifosato es de al menos aproximadamente 1.2.

20.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación en peso de glifosato, a.e., con respecto a la suma de sal(es) de alquilamonio cuaternario alcoxilado se encuentra entre aproximadamente 3 y aproximadamente 20.

21.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 20, caracterizado además porque la relación en peso de glifosato, a.e., con respecto a la suma de sal(es) de alquilamonio

H
117

cuaternario alcoxilado se encuentra entre aproximadamente 3 y aproximadamente 10.

22.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la
5 concentración de la suma de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario alcoxilado se encuentra entre aproximadamente 3% en peso y aproximadamente 12% en peso.

23.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 22, caracterizado además porque la
10 concentración de la suma de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario alcoxilado se encuentra entre aproximadamente 3.5% en peso a aproximadamente 10% en peso.

24.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque tiene una
15 clasificación de amarilla en la toxicidad al ojo en banda roja.

25.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque comprende una sal de amonio del glifosato y contiene más de 38.0% en peso/L de glifosato a.e., al menos un agente tensioactivo de sal de alquilamonio
20 cuaternario alcoxilado en donde cada uno de p, q, p' y q' es independientemente un entero entre 0 y 3, dicho concentrado tiene un pH <7.3.

118

26.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 25, caracterizado además porque dicho concentrado tiene una concentración de amoníaco en la solución que es menor de aproximadamente 750 ppm a 25°C.

5 27.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación el peso del total de agente tensioactivo(s) de alquilamonio cuaternario alcoxilado con respecto al glifosato de amonio del ión de alquilamonio cuaternarios alcoxilado en dicho concentrado siendo no mayor de
10 aproximadamente 0.28.

28.- El concentrado líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque la concentración molar de dicho agente tensioactivo de sal de alquilamonio cuaternario alcoxilado no es mayor de aproximadamente 0.15.

15 29.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque R comprende entre aproximadamente 8 y aproximadamente 18 átomos de carbono.

20 30.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 29, caracterizado además porque R se deriva predominantemente a partir de sebo.

31.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 28, caracterizado además porque la relación

en peso de la suma de todos esos agentes tensioactivos de sal de alquilamonio cuaternario alcoxilado con respecto a la suma de cualesquiera de los agentes tensioactivos no iónicos es mayor de 4.5:1.

5 32.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxilado con respecto a la suma de cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileo es mayor de 5.2:1.

10 33.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 32, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxilado con respecto la suma de cualesquiera agentes tensioactivos no iónicos es mayor de 5.2:1.

15 34.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 32, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxilado con respecto a la suma de cualesquiera agentes tensioactivos de alquil éter de óxido de polialquileo es mayor de
20 10:1.

35.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 34, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de

~~118~~
120

alquilamonio cuaternario alcoxlado con respecto la suma de cualesquiera agentes tensioactivos no iónicos es mayor de 10:1.

36.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque
5 comprende al menos aproximadamente 325 gpl de glifosato, a.e.

37.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 36, caracterizado además porque comprende al menos aproximadamente 360 g/L de glifosato, a.e.

38.- El concentrado herbicida líquido acuoso estable de
10 conformidad con la reivindicación 37, caracterizado además porque comprende al menos aproximadamente 400 g/L de glifosato, a.e.

39.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque contiene no más de aproximadamente 5% en peso de sulfato de amonio.

15 40.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque la relación de la suma de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario dialcoxilado con respecto a la suma de (alquilen glicol(es) + Alquilen éter glicol(es)) es mayor de aproximadamente 3.25.

20 41.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque la relación de la suma de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario

dialcoxilado con respecto a la suma de (alquilen glicol(es) + alquilen éter glicol(es)) es mayor de aproximadamente 4.

42.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque tiene una
5 clasificación de amarilla en la toxicidad al ojo en banda roja.

43.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizado además porque la concentración molar del ión de alquilamonio cuaternario alcoxilado no es mayor de aproximadamente 0.13.

10 44.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 27, caracterizada además porque la concentración molar total de todos los iones de amonio cuaternario no es mayor de aproximadamente 0.15.

15 45.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 1, caracterizado además porque la relación en peso del total de agente(s) tensioactivo(s) de alquilamonio cuaternario alcoxilado con respecto al glifosato de amonio, a.e., en dicho concentrado siendo de entre aproximadamente 0.1:1 y aproximadamente 0.2:1, y el número promedio del valor de $(p + p' + q + q' + z + z')$ para dicho al menos un
20 agente tensioactivo se encuentra entre aproximadamente 2 y aproximadamente 10.

46.- Un concentrado herbicida líquido acuoso estable que comprende un sal de amonio del glifosato y que contiene al menos

122

aproximadamente 120 g/L de glifosato a.e., ión de amonio en una relación molar de glifosato entre aproximadamente 0.75 y aproximadamente 2.5, y al menos un agente tensioactivo de sal de alquilamonio cuaternario alcoxlado que corresponde a la fórmula: $RR'N^{(+) }AB$; en donde R es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, A es $(R^2O)p(R^3O)q(R^4O)zR^8$ y B es $(R^5O)p'(R^6O)q'(R^7O)z'R^9$ en donde cada uno de R^2 , R^3 , R^4 , R^5 , R^6 , y R^7 se selecciona independientemente a partir del grupo que consiste de etileno e isopropileno, cada uno de p, q, p', q', z y z' es independientemente un entero entre 0 y 30 y la suma de $[p + p' + q + q' + z + z']$ es al menos aproximadamente 2, la relación en peso del total de agentes tensioactivos de alquilamonio cuaternario del alquilo alcoxlado con respecto al glifosato de amonio, a.e., en dicho concentrado siendo entre aproximadamente 0.1:1 y aproximadamente 0.2:1, y el valor promedio de $(p+p'+q+q'+z+z')$ para dicho al menos un agente tensioactivo es entre aproximadamente 3 y aproximadamente 10.

47.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 46, caracterizado además porque el valor promedio de $(p+p'+q+q'+z+z')$ para dicho al menos un agente tensioactivo es entre aproximadamente 3 y aproximadamente 8.

48.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 46, caracterizado además porque el valor promedio de

723

($p+p'+q+q'+z+z'$) para dicho al menos un agente tensioactivo es entre aproximadamente 4 y aproximadamente 8.

49.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 46, caracterizado además porque el valor promedio de ($p+p'+q+q'+z+z'$) para dicho al menos un agente tensioactivo es entre aproximadamente 5 y aproximadamente 10.

50.- Un concentrado herbicida líquido acuoso estable que comprende una sal de amonio del glifosato y que contiene al menos aproximadamente 120 gramos/L de glifosato a.e., ión de amonio en una relación molar de con respecto al glifosato entre aproximadamente 0.75 y aproximadamente 2.5, y al menos dos agentes tensioactivos de sal de alquilamonio cuaternario alcoxilado que corresponden a la fórmula: $RR'N^{(+)}AB$; en donde R es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 8 a 22 átomos de carbono, R' es un grupo alquilo saturado o no saturado, de cadena recta o ramificada que tiene de 1 a 4 átomos de carbono, A es $(R^2O)p(R^3O)q(R^4O)zR^6$ y B es $(R^5O)p'(R^6O)q'(R^7O)z'R^8$ en donde cada uno de R^2 , R^3 , R^4 , R^5 , R^6 , y R^7 se selecciona independientemente a partir del grupo que consiste de etileno e isopropileno, y cada uno de p, q, p', q', z y z' es independientemente un entero entre 0 y 30 y la suma de $[p + p' + q + q' + z + z']$ es al menos aproximadamente 2, la relación en peso del total de agentes tensioactivos de alquilamonio cuaternario del alquilo alcoxilado con respecto al glifosato de amonio, a.e., en dicho concentrado siendo entre aproximadamente 0.1:1 y

123
124

aproximadamente 0.2:1, y el valor promedio de $(p+p'+q+q'+z+z')$ para dicho al menos dos agentes tensioactivos siendo entre aproximadamente 2 y aproximadamente 5, y la suma promedio de $(p+p'+q+q'+z+z')$ para otros de dichos al menos dos agentes tensioactivos siendo entre aproximadamente 5 y aproximadamente 15.

51.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 50, caracterizado además porque la relación en peso de la suma de dicho uno y dicho otro agentes tensioactivos con respecto a glifosato de amonio, a.e., es de entre aproximadamente 0.1:1 y aproximadamente 0.2:1.

52.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 51, caracterizado además porque la relación en peso de dicho un agente tensioactivo con respecto a dicho otro agente tensioactivo se encuentra entre aproximadamente 1:1.5 y aproximadamente 1.5:1.

53.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 50, caracterizado además porque la relación molar de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario alcoxlado con respecto al glifosato no es mayor de aproximadamente 0.2:1.

54.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 50, caracterizado además porque la relación en peso de agente(s) tensioactivo(s) de sal de alquilamonio cuaternario alcoxlado con respecto al glifosato se encuentra entre aproximadamente 0.1:1 y aproximadamente 0.17:1.

55.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 50, caracterizado además porque la concentración molar del ión de alquilamonio cuaternario alcoxlado en dicho concentrado acuoso no es mayor de aproximadamente 0.15.

5 56.- El concentrado herbicida líquido acuoso de conformidad con la reivindicación 50, caracterizado además porque la concentración molar total de todos los iones de amonio cuaternario no es mayor de aproximadamente 0.15.

10 57.- Un concentrado herbicida líquido acuoso estable que comprende una sal de amonio del glifosato que contiene al menos aproximadamente 240 g/L de glifosato a.e., ión de amonio en una relación molar con respecto al glifosato entre aproximadamente 0.8 y aproximadamente 2.5, y al menos un agente tensioactivo de sal del alquilamonio cuaternario alcoxlado predominantemente que comprende un
15 sustituyente N-alquilo derivado a partir de sebo.

58.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque la relación en peso de la suma de todos esos agentes tensioactivos de la sal de alquilamonio cuaternario alcoxlado con respecto la suma de cualesquiera
20 agentes tensioactivos de alquil éter de óxido de polialquileo es mayor de 4.5:1.

~~128~~
126

59.- El concentrado herbicida líquido acuoso estable de conformidad con la reivindicación 57, caracterizado además porque comprende al menos aproximadamente 325 gpl de glifosato, a.e.

PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL SEARCHING AUTHORITY

To:
AKZO NOBEL INC.
Intellectual Property Dept.
Attn: Mancini, Ralph J.
7 Livingstone Avenue
Dobbs Ferry, NY 10522
UNITED STATES OF AMERICA

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT AND
THE WRITTEN OPINION OF THE INTERNATIONAL
SEARCHING AUTHORITY, OR THE DECLARATION

AKZO NOBEL INC.

FEB 08 2006

INTELLECTUAL PROPERTY DEPT.

(PCT Rule 44.1)

Scanned
2/8/06
CWA

Applicant's or agent's file reference ACA6355WO	FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No. PCT/US2005/034076	International filing date (day/month/year) 23/09/2005
Applicant ZHU, Shao	

- ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.
Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 48):
When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.
Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 338.82.70
For more detailed instructions, see the notes on the accompanying sheet.
- ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.
- ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.
☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.
- Reminders**
Shortly after the expiration of 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.2, respectively, before the completion of the technical preparations for international publication.
The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.
Within 18 months from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later); otherwise, the applicant must, within 30 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.
In respect of other designated Offices, the time limit of 30 months (or later) will apply even if no demand is filed within 18 months.
See the Annex to Form PCT/IS901 and, for details about the applicable time limits, Office by Office, see the PCT Applicant's Guide, Volume II, National Chapters and the WIPO internet site.

Name and mailing address of the International Searching Authority

European Patent Office, P.O. Box 5516 Palantien 2
NL-2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx: 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Sandrine Parriche

Form PCT/IS901 (January 2004)

(See notes on accompanying sheet)

FDJ
708

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under Article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report and the written opinion of the International Searching Authority, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the letter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only (see *PCT Applicant's Guide*, Annexes B1 and B2).

The attention of the applicant is drawn to the fact that amendments to the claims under Article 19 are not allowed where the International Searching Authority has declared, under Article 17(2), that no international search report would be established (see *PCT Applicant's Guide*, Volume IA, paragraph 288).

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 18 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 18(1)" (see below, under "Statement under Article 18(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

720
129

~ PATENT COOPERATION TREATY ~

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference ACA535510	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, Item 5 below.	
International application No. PCT/082005/034076	International filing date (day/month/year) 23/09/2005	(Earliest) Priority Date (day/month/year) 23/09/2004
Applicant SHU, Shawn		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 6 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

2. ☐ Certain claims were found unsearchable (See Box II).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ The text has been established, according to Rule 36.2(b), by this Authority as it appears in Box No. (V). The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the drawings,

a. the figure of the drawings to be published with the abstract is Figure No. _____

☐ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

126
130

PL./US2005/034076

A. CLASSIFICATION OF SUBJECT MATTER A01N57/20 A01N25/30 A01P13/00 //(A01N57/20,25:30)		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) A01N Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94/02021 A (MONSANTO COMPANY) 3 February 1994 (1994-02-03) page 2, line 23 - page 3, line 1 page 3, lines 22-36 page 4, lines 3-24, 34-37 page 6, lines 10-33 page 8, lines 2-19; examples 1-5 -/-	1-19, 23-87
☒ Further documents are listed in the continuation of item C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claims or which is cited to establish the publication date of another claim or other special reason (see definition) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to substantiate the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "U" document member of the same patent family		
Date of the actual completion of the international search 27 January 2006		Date of mailing of the international search report 06/02/2006
Name and mailing address of the ISA/ European Patent Office, P.O. Box 6016 Patentstr. 2 NL - 3720 BZ Utrecht Tel. (+31-70) 340-3340, Tx. 31 651 600 01, Fax. (+31-70) 340-3016		Authorized officer Klaever, J

3

138
137

PL./US2005/034076

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 998 332 A (SATO ET AL) 7 December 1999 (1999-12-07) cited in the application column 2, lines 1-35 column 3, lines 7-22, 38-50 column 4, lines 36-49 column 4, line 66 - column 5, line 7 column 5, line 48 - column 6, line 10 column 8, lines 17-19, 38-41 column 9, lines 35-57 column 10, lines 40-43 column 11, line 40 - column 12, line 9 column 15, lines 24-47; examples 1-7, 12, 19-21	1, 6-19, 23, 24, 29-62, 67-87
X	EP 0 582 561 A (MONSANTO COMPANY) 9 February 1994 (1994-02-09) page 3, lines 46-54 page 5, lines 17-24, 40-42; example 3	1-21
X	EP 0 274 369 A (MONSANTO COMPANY) 13 July 1988 (1988-07-13) page 2, lines 26-29 page 2, line 59 - page 3, line 22 page 3, lines 60-62; example I	1-13, 16-19
P, X	WO 2005/016002 A (DOW AGROSCIENCES LLC) 24 February 2005 (2005-02-24) page 3, lines 11-20 page 4, line 7 - page 5, line 12 page 10, lines 5-11, 20-22; example 1; table 1	1-10, 12, 13, 16-19
X	WYRILL J B ET AL: "GLYPHOSATE TOXICITY TO COMMON MILKWEED AND HEMP DOGBANE AS INFLUENCED BY SURFACTANTS" WEED SCIENCE, WEED SCIENCE SOCIETY OF AMERICA, CHAMPAIGN, IL, US, vol. 25, no. 3, May 1977 (1977-05), pages 275-287, XP002034447 ISSN: 0043-1745 page 278, column 1, paragraph 2 page 279, column 2, paragraph 1 table 5 page 284, column 1, paragraph 2; tables 7, 8	1-11, 13-15, 18, 19
-/-		

181
132

P.../US2005/034076

Continuation. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	P. E. LAERKE & J. C. STREIBIG: "Foliar absorption of some glyphosate formulations and their efficacy on plants" PESTIC. SCI., vol. 44, 1995, pages 107-116, XP009060636 page 108, column 1, paragraph 6 - column 2, paragraph 1; table 1 page 109, column 1, paragraph 1 page 111, column 1, paragraph 1 page 114, column 1, paragraph 1 page 114, column 2, paragraph 4	1-9, 11, 13-15
X	EP 0 526 444 A (MONSANTO COMPANY) 3 February 1993 (1993-02-03) page 2, line 43 - page 3, line 11 page 3, lines 45-58 page 4, lines 6-13, 43-50; examples 1-14	1-9, 11-13, 16, 17
X	US 5 462 912 A (HIOKI ET AL) 31 October 1995 (1995-10-31) column 2, line 64 - column 3, line 60 column 5, lines 10-27 column 6, lines 23-27 column 7, lines 62-67 column 9, lines 24-52; examples 1, 4, 5; tables 1A, 1B, 4A-5B	1-11, 13-22
X	WO 97/32476 A (KAO CORPORATION; MONSANTO COMPANY; OKANO, TETSUYA; HASEBE, KEIKO; SUZU) 12 September 1997 (1997-09-12) page 3, paragraph 2 page 7, paragraphs 2, 3 page 10, paragraph 4 - page 12, paragraph 1 page 14, paragraph 2 page 16, paragraph 2 compound (4) table 1 tables 3, 6-8	1, 2, 6-9, 11-14, 16, 17, 22

132
133

Information on patent family members

PL., US2005/034076

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9402021 A	03-02-1994	AT 179302 T	15-05-1999
		AU 676482 B2	13-03-1997
		AU 4412193 A	14-02-1994
		BR 9306732 A	08-12-1998
		CA 2137281 A1	03-02-1994
		DE 69324683 D1	02-06-1999
		DE 69324683 T2	25-11-1999
		EP 0650326 A1	03-05-1995
		JP 7509700 T	26-10-1995
		KR 159995 B1	16-11-1998
		MX 9304300 A1	31-01-1994
		NZ 253632 A	29-01-1997
		US 5317003 A	31-05-1994
US 5998332 A	07-12-1999	AT 251383 T	15-10-2003
		AU 732689 B2	26-04-2001
		AU 8582698 A	16-02-1999
		BR 9810811 A	12-09-2000
		CA 2297036 A1	04-02-1999
		CN 1115961 C	30-07-2003
		DE 69818829 D1	13-11-2003
		DE 69818829 T2	05-08-2004
		DK 999749 T3	16-02-2004
		EP 0999749 A1	17-05-2000
		ES 2209171 T3	16-06-2004
		HU 0002407 A2	28-11-2000
		JP 2001510776 T	07-08-2001
		NO 20000292 A	22-03-2000
		NZ 502397 A	26-04-2002
		PL 338233 A1	09-10-2000
		SK 772000 A3	14-08-2000
		TR 200000191 T2	21-08-2000
		TW 492843 B	01-07-2002
		UA 66365 C2	15-12-2000
		WO 9904635 A1	04-02-1999
		ZA 9806502 A	04-02-1999
EP 0582561 A	09-02-1994	AU 4432493 A	03-02-1994
		CA 2101669 A1	01-02-1994
		JP 6256121 A	13-09-1994
		NZ 248289 A	24-02-1995
		US 5612285 A	18-03-1997
		US 5693593 A	02-12-1997
EP 0274369 A	13-07-1988	AU 595406 B2	29-03-1990
		AU 8204587 A	09-06-1988
		DE 3764945 D1	18-10-1990
		DK 635087 A	05-06-1988
		GR 3000911 T3	10-12-1991
		IE 61324 B1	02-11-1994
		JP 1983027 C	25-10-1995
		JP 7002608 B	18-01-1995
		JP 63145205 A	17-06-1988
		KR 9200862 B1	30-01-1992
		NZ 222796 A	27-03-1990
WO 2005016002 A	24-02-2005	NONE	

128
134

Information on patent family members

PC 1, US2005/034076

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0526444	A	03-02-1993	AT 146035 T	15-12-1996
			AU 648919 B2	05-05-1994
			AU 2066192 A	04-02-1993
			BR 9202963 A	30-03-1993
			CA 2075004 A1	03-02-1993
			DE 69215785 D1	23-01-1997
			DE 69215785 T2	26-06-1997
			JP 6024917 A	01-02-1994
			MX 9204470 A1	01-05-1993
			NZ 243780 A	23-12-1993
			US 5430005 A	04-07-1995
			ZA 9205731 A	05-11-1993
US 5462912	A	31-10-1995	NONE	
WO 9732476	A	12-09-1997	AU 713956 B2	16-12-1999
			AU 2231597 A	22-09-1997
			BR 9702106 A	12-01-1999
			CN 1190327 A	12-08-1998
			DE 69713557 D1	01-08-2002
			DE 69713557 T2	09-01-2003
			EP 0824315 A1	25-02-1998
			ES 2175349 T3	16-11-2002
			ID 16129 A	04-09-1997
			NZ 328990 A	29-06-1999
			US 5948421 A	07-09-1999

135
135

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43b/s.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No. PCT/US2005/034076	International filing date (day/month/year) 23.09.2005	Priority date (day/month/year) 23.09.2004
--	--	--

International Patent Classification (IPC) or both national classification and IPC
A01N57/20, A01N25/80, A01P13/00

Applicant
ZHU, Shawn

1. This opinion contains indications relating to the following items:
- ☒ Box No. I Basis of the opinion
 - ☒ Box No. II Priority
 - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - ☐ Box No. IV Lack of unity of invention
 - ☒ Box No. V Reasoned statement under Rule 43b/s.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - ☒ Box No. VI Certain documents cited
 - ☒ Box No. VII Certain defects in the international application
 - ☒ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA"). However, this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 86.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of three months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:  European Patent Office D-80589 Munich Tel. +49 89 2369 - 0 Tx: 623658 epnu d Fax: +49 89 2369 - 4465	Authorized Officer Klever, J Telephone No. +49 89 2369-6801
--	---



135
136

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/US2005/034078

Box No. I Basis of the opinion

1. With regard to the language, this opinion has been established on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
 - ☐ This opinion has been established on the basis of a translation from the original language into the following language , which is the language of a translation furnished for the purposes of international search (under Rules 12.3 and 23.1(b)).
2. With regard to any nucleotide and/or amino acid sequence disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material:
 - ☐ a sequence listing
 - ☐ table(s) related to the sequence listing
 - b. format of material:
 - ☐ in written format
 - ☐ in computer readable form
 - c. time of filing/furnishing:
 - ☐ contained in the international application as filed.
 - ☐ filed together with the international application in computer readable form.
 - ☐ furnished subsequently to this Authority for the purposes of search.
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. II Priority

1. ☒ The validity of the priority claim has not been considered because the International Searching Authority does not have in its possession a copy of the earlier application whose priority has been claimed or, where required, a translation of that earlier application. This opinion has nevertheless been established on the assumption that the relevant date (Rules 43bis.1 and 64.1) is the claimed priority date.
2. ☐ This opinion has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid (Rules 43bis.1 and 64.1). Thus for the purposes of this opinion, the international filing date indicated above is considered to be the relevant date.
3. Additional observations, if necessary:

12/0
137

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/US2005/034078

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	
	No: Claims	1-87
Inventive step (IS)	Yes: Claims	
	No: Claims	1-87 (insofar as novel)
Industrial applicability (IA)	Yes: Claims	1-87
	No: Claims	

2. Citations and explanations

see separate sheet

Box No. VI Certain documents cited

1. Certain published documents (Rules 43bis.1 and 70.10)

and /or

2. Non-written disclosures (Rules 43bis.1 and 70.9)

see form 210

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

International application No.

PCT/US2005/034076

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1). The subject-matter of claims 1 - 22 is not novel (Art. 33 (2) PCT) for the following reasons:

Herbicidal formulations comprising alkoxyated quaternary ammonium cationic surfactants have been disclosed in all documents cited in the International Search Report (ISR), for references in the cited documents it is referred to the passages as cited in the ISR:

WO 94/02021 A1 (= D1) discloses aqueous concentrates comprising 5 - 40% of a glyphosate salt and a cationic surfactant within the scope of Formula I of claim 18, resulting in low eye irritancy and very low fish toxicity. The ratio of surfactant to glyphosate may vary in wide ranges and is preferably between 1 : 5 and 5 : 1. The presence of further surfactants is optional and the examples in Table 1 do not contain any further surfactant. The presence of glycol is (advantageously) not required but may be added if desired. The presence of a co-herbicide such as 2,4-D, dicamba or acifluorfen also is mentioned in D1. D1 hence anticipates the subject-matter of present claims 1 - 13 and 16 - 19.

US 5,998,332 (= D2) discloses aqueous concentrates comprising 300 - 800 g/L ammonium glyphosate and quaternary alkyl ammonium surfactants within the scope of Formula I of claim 18, in particular methyl bis (2-hydroxyethyl)coco ammonium chloride, and polyoxyethylene alkanol as nonionic surfactant. The presence of co-herbicides and glycol also has been disclosed in D2.

D2 hence anticipates the subject-matter of present claims 1 and 6 - 19.

EP 582 561 A1 (= D3) discloses solid compositions comprising glyphosate, a surfactant which preferably is a cationic surfactant such as Ethoquad C/25 or 18/25 and an extrusion aid which is a polyethylene glycol. The presence of co-herbicides also is disclosed in D3. D3 hence anticipates the subject-matter of present claims 1 - 9, 11 - 13, 16 - 18, 20 and 21.

EP 274 369 A1 (= D4) discloses aqueous concentrates of ammonium glyphosate, ammonium sulfate and alkoxyated quaternary alkyl ammonium salts as surfactants, which optionally may contain further (nonionic) surfactants. D4 and in particular the concentrate as disclosed in Example I anticipates the subject-matter of present claims 1 - 8, 10 - 13, 18 and 19.

Wyrill & Burnside, 1977 (= D6) disclose aqueous formulations of glyphosate and various

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

International application No.

PCT/US2005/034078

surfactants including Ethoquads within the scope of present claims 10, 18 and 19. D6 anticipates the subject-matter of claims 1 - 8, 10, 11, 13 - 15, 18 and 19.

Laerke & Strelbig, 1995 (= D7) disclose aqueous glyphosate formulations comprising as cationic surfactant the ethoxylated trimethyl quaternary ammonium compound Trimao hence anticipating the subject-matter of claims 1 - 8, 11 and 13 - 15.

EP 526 444 A1 (= D8) discloses aqueous glyphosate formulations comprising alkoxyated lower alkyl quaternary ammonium salts, preferably in combination with glycol, which possess a low eye irritancy and low toxicity.

D8 hence anticipates the novelty of present claims 1 - 9, 11 - 13, 16 and 17.

US 5,462,912 (= D9) discloses herbicidal compositions, including solid compositions, comprising a herbicide such as glyphosate, paraquat or glufosinate with an alkoxyated alkyl quaternary ammonium salt within the scope of Formula I of claim 18.

D9 hence anticipates the novelty of claims 1 - 8, 11 and 13 - 18 and 20 - 22.

WO 97/32476 A1 (= D10) discloses herbicidal formulations comprising a herbicide such as glyphosate or glufosinate and an alkoxyated alkyl quaternary ammonium salt in combination with a nonionic amine based surfactant, thus anticipating the novelty of present claims 1, 2, 6 - 9, 11 - 14, 16, 17 and 22.

2). The subject-matter of claims 23 - 87 is not novel (Art. 33 (2) PCT) for the following reasons:

The disclosure of D1 is directed at the formulation of aqueous concentrates of glyphosate salts, including ammonium salts, and teaches that cationic polyoxyethylene/propylene alkyl quaternary ammonium surfactants within the scope of the formula $RR'N^{+}AB$ as defined in present claim 23 may be advantageously used to obtain concentrates having a low eye irritancy. The aqueous concentrates of D1 do neither contain nonionic surfactants nor ammonium sulfate.

D1 hence anticipates the subject-matter of claims 23 - 87. Insofar as some claims define features that have not been specifically disclosed in D1, it concerns random selections from the various possibilities that have been disclosed in D1. The molar ratio of ammonium as defined by claims 43/44 is normally obtained when one selects the ammonium salt from the (narrow) range of possible salts indicated in D1, whereas the tallow-derived R-group is well within the range of the C_8 to C_{20} alkyl groups of surfactant (b) of D1.

In following the teachings of D1, the skilled artisan automatically and necessarily will arrive

198
140

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

International application No.
PCT/US2005/034076

at the formulations as defined by present claims 23 - 87.

It can furthermore not be seen from the application documents on file which particular technical problem has been solved in a non-obvious way by the formulations as defined by the present claims. The advantageous effect of the alkoxyated quaternary ammonium surfactants as used in the present application on aqueous glyphosate concentrates is known from D1 and there is no apparent reason why the skilled artisan would hesitate to apply these surfactants to ammonium salts of glyphosate, which are explicitly mentioned in D1.

So even if the subject-matter of claims 1 - 87 would be considered novel, they are not considered to be based on an inventive step (Art. 33 (3) PCT).

Re Item VI

Certain documents cited

Certain published documents

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO 2005/016002	24.02.05	06.02.04	04.08.03 US

Provided that the present application validly claims the priority date of 23.08.04 US, this document (D5 of the ISR) does not form part of the prior art (Rule 64.1 (b)(ii) PCT).

D5 discloses herbicidal formulations comprising monomethyl and dimethyl amine salts of glyphosate and a alkoxyated quaternary ammonium surfactant within the scope of formula I of present claim 18 in particular the surfactants Ethoquad C/12 and 18/12 (D5: page 5, line 3 - 12, page 10, line 10/11 and Formulation References 2 and 3 in Table 1). The presence of further ingredients such as glycols or co-herbicides also has been disclosed in D5 (page 11, line 17 - 24). In the European phase of the application D5 hence will be relevant prior art for the purposes of Art. 54 (3) EPC for claims 1 - 10, 12, 13 and 16 - 19.

Re Item VII

Certain defects in the international application

- Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed

147

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING
AUTHORITY (SEPARATE SHEET)**

International application No.

PCT/US2005/034076

in the documents D1, D3, D8 and D9 is not mentioned in the description, nor are these documents identified therein.

- The number of claims is not reasonable in consideration of the nature of the invention (Rule 6.1(a) PCT).

Re Item VIII

Certain observations on the international application

The number of claims taken in combination with the slight variations between the independent composition claims 23, 51, 57 and 77 results in an ambiguously defined scope of protection contrary to the requirements of Art. 8 PCT.

For example, the alkoxyated cationic surfactant of (Independent) claim 51 has not been restricted to the surfactant as used in the concentrate defined by claim 23. Claim 51 does not contain the limiting feature with respect to the nonionic surfactant. This claim hence is much broader than claim 23, apart from the tallow-feature.

Claim 77 is essentially identical with claim 57, apart from the maximum molar concentration featuring in claim 57. It thus appears, that claims 57 - 76 actually should be dependent on claim 77.

It is furthermore pointed out, that various dependent claims are not grouped together in the most practical way possible and in some cases define a broader scope than the independent claims to which they refer (e. g. claims 54 - 56, with claim 55 defining a minimum cationic surfactant/alkylether surfactant below that of independent claim 23).

142

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

INVITATION TO
SUBMIT AMENDMENTS

(PCT Rule 60.1(a))

To:

RALPH J. MANCINI
AKZO NOBEL INC.
INTELLECTUAL PROPERTY DEPARTMENT
7 LIVINGSTONE AVENUE
DOBBS FERRY, NEW YORK 10522-3408

Date of mailing
(day/month/year)

15 Aug 2008

Applicant's or agent's file reference

ACA8355WO

REPLY DUE

within month/days from
the above date of mailing

International application No.

International filing date
(day/month/year)

23 Sep 2005

Applicant

AKZO NOBEL N.V.

1. The applicant is hereby invited, within the time limit indicated above, to submit to this International Preliminary Examining Authority the following documents which were referred to in the statement concerning amendments made in the demand for international preliminary examination, but not attached to the demand:

☒ amendments made under Article 34 of

☐ the description

☒ the claims

☐ the drawings

☐ letter accompanying amendments under Article 34.

2. If the documents are submitted to this Authority within the time limit indicated above, they will be taken into account for the start of the international preliminary examination (Rule 69.1(c)).

3. If the documents are not submitted to this Authority within the time limit indicated above, the international preliminary examination may start without taking them into account (Rule 66.4(b)).

Name and mailing address of the IPEA/

Mail Stop PCT, Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450
Facsimile No. 571-276-3207

Authorized officer

Nhu Thuy Tran

Telephone No. 703-308-8290 EX 105

~~143~~
143

EV654633223US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Akzo Nobel N.V.
Inventor(s): Zhu et al.
Serial No. PCT/US2005/034076
Filed: September 23, 2005
For: ALKOXYLATED ALKYLAMINE QUATERNARY SURFACTANTS FOR
GLYPHOSATE
Atty. Ref.: ACA6355WO (MTC 6920.8)

September 12, 2006

RESPONSE TO INVITATION TO SUBMIT AMENDMENTS

COMMISSIONER FOR PATENTS,
Attn: Authorized Officer Nhu Thuy Tran

Dear Officer Tran:

In response to the Invitation to Submit Amendments dated August 15, 2006
(copy enclosed), Applicant submits amendments under Article 34.

Applicant respectfully requests that International preliminary examination start
on the basis of the claims as amended under Article 34 as set forth in the
accompanying replacement pages (PCT Rule 69.1(e)) and that an Examination
Report be issued for the above-referenced PCT application.

Respectfully submitted,



Andrew C. Wegman, Reg. No. 54,530
SENNIGER POWERS
One Metropolitan Square, 16th Floor
St. Louis, Missouri 63102
(314) 231-5400

ACW/dll
Express Mail Label No. EV 654633223 US
Mail Stop PCT

148
744

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

AKZO NOBEL INC.

AUG 24 2006

PCT

INTELLECTUAL PROPERTY DEPARTMENT

To:

RALPH J. MANCINI
AKZO NOBEL INC.
INTELLECTUAL PROPERTY DEPARTMENT
7 LIVINGSTONE AVENUE
DOBBS FERRY, NEW YORK 10522-3408

NOTIFICATION OF RECEIPT
OF DEMAND BY COMPETENT INTERNATIONAL
PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing
(day/month/year)

15 Aug 2006

Applicant's or agent's file reference

ACA6355WO

IMPORTANT NOTIFICATION

International application no.

PCT/US2005/034076

International filing date (day/month/year)

23 Sep 2005

Priority date (day/month/year)

23 Sep 2004

Applicant

AKZO NOBEL N.V.

- 1 The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

24 Jul 2006

- 2 That date of receipt is

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

- 3 ☐ **ATTENTION:** That date of receipt is after the expiration of 19 months from the priority date. Consequently, in respect of some Offices, the demand does not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)) and the acts for entry into the national phase must therefore be performed within 20 months from the priority date (or later in some Offices). However, in respect of some other Offices, the time limit of 30 months (or later) may nevertheless apply. See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on

- 4 Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/
Mail Stop PCT, Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450
Facsimile No. 571-273-3201

Authorized officer

Nhu Thuy Tran

Telephone No. 703-308-9290 EX 105

2006
1/1

144
145

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

INVITATION TO
SUBMIT AMENDMENTS

(PCT Rule 60.1(g))

To: RALPH J. MANCINI AKZO NOBEL INC. INTELLECTUAL PROPERTY DEPARTMENT 7 LIVINGSTONE AVENUE DOBBS FERRY, NEW YORK 10522-3408		Date of mailing (day/month/year) 15 Aug 2006
Applicant's or agent's file reference ACA8355WO		REPLY DUE within months/days from the above date of mailing
International application No		International filing date (day/month/year) 23 Sep 2005
Applicant AKZO NOBEL N.V.		

1. The applicant is hereby invited, within the time limit indicated above, to submit to this International Preliminary Examining Authority the following documents which were referred to in the statement concerning amendments made in the demand for international preliminary examination, but not attached to the demand:

☒ amendments made under Article 34 of

☐ the description

☒ the claims

☐ the drawings

☐ letter accompanying amendments under Article 34.

2. If the documents are submitted to this Authority within the time limit indicated above, they will be taken into account for the start of the international preliminary examination (Rule 69.1(c)).

3. If the documents are not submitted to this Authority within the time limit indicated above, the international preliminary examination may start without taking them into account (Rule 66.4bis).

Name and mailing address of the IPEA/ Mail Stop PCT, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No 571-273-3207	Authorized officer Nhu Thuy Tran Telephone No 703-308-9290 EX 105
---	---

Form PCT/IPEA431 (July 1992; reprint January 2004)

ACA6355WO (MTC 6920.8)
PCT

1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Akzo Nobel Inc.
Inventor(s): Zhu et al.
Application No.: PCT/US2005/034076
Filed: September 23, 2005
For: ALKOXYLATED ALKYLAMINE QUATERNARY
SURFACTANTS FOR GLYPHOSATE
Applicant's Ref.: ACA6355WO (MTC 6920.8)

September 12, 2006

AMENDMENT PURSUANT TO ARTICLE 34

This Amendment pursuant to Article 34 PCT is presented in connection with the Demand for International Preliminary Examination filed July 24, 2006, pursuant to PCT Rule 69.1, and in response to the Invitation to Submit Amendments dated August 15, 2006.

* Enclosed are replacement pages 21 to 33 reflecting amendments to the claims. Claim 1 has been amended to more clearly define the invention and more clearly distinguish the prior art. Original claims 57 and 77 (now claims 48 and 66, respectively) have been amended to depend from original claim 23 (now claim 15). New independent claims 77 and 81 correspond to original dependent claims 78 and 81, respectively.

Item V (Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanation supporting such statement)

Applicant respectfully submits that the pending claims are novel and involve an inventive step over the cited references for the reasons set forth below.

~~146~~
147

I. Claims 23-87

In accordance with the instant amendment, the subject matter of original claims 23-87 is now presented with appropriate amendments in claims 15-87.

Claim 15

Independent claim 15 (original claim 23) is directed to a stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and an alkoxyated quaternary alkyl ammonium salt, in which the weight ratio of the sum of all alkoxyated quaternary alkyl ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) present in the formulation is greater than 4.5:1.

More particularly, claim 15 is directed to such an herbicidal concentrate containing at least about 240 g/L glyphosate, a.e., in which the molar ratio of ammonium ion to glyphosate is between about 0.8 and about 2.5. The concentrate comprises at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula $RR'N^{(+)}AB$. R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ and B is $(R^5O)_p'(R^6O)_q'(R^7O)_z'R^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, each of R^8 and R^9 is selected from the group consisting of hydrogen, methyl and ethyl, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $p + p' + q + q' + z + z'$ is at least about 2.

~~147~~
748

Claim 43

Independent claim 43 (original claim 51) is directed to a stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and at least one alkoxyated quaternary alkylammonium salt surfactant predominantly comprising an N-alkyl substituent derived from tallow. The ammonium ion to glyphosate molar ratio is between about 0.8 and about 2.5 and the concentrate contains glyphosate at a concentration of at least about 240 g/L glyphosate, a.e.

Claims 77 and 81

New independent claims 77 and 81 (original dependent claims 78 and 81, respectively) are directed to stable aqueous liquid herbicidal concentrates comprising an ammonium salt of glyphosate and least one alkoxyated quaternary alkylammonium salt surfactant (claim 77) or at least two alkoxyated quaternary alkylammonium salt surfactants (claim 81) of the formula $RR'N^{(+)AB}$ defined above in the formulation of claim 15.

In the concentrate of claim 77, the average value of $(p + p' + q + q' + z + z')$ for at least one surfactant is between about 3 and about 10.

In the concentrate of claim 81, the average sum of $(p + p' + q + q' + z + z')$ for one of the at least two surfactants is about 2 and about 5, and the average sum of $(p + p' + q + q' + z + z')$ for another of the at least two surfactants is between about 5 and about 15.

As specified in both claims 77 and 81, the concentrates contain at least about 120 g/L glyphosate, a.e., the ammonium ion to glyphosate molar ratio is between about 0.75 and about 2.5, and the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., is between about 0.1:1 and about 0.2:1.

4483
749

State of the Art

N-phosphonomethylglycine (glyphosate) is well-known in the art as an effective post-emergent foliar applied herbicide. Since the acid form is substantially insoluble in water, glyphosate is generally formulated and applied as a water soluble salt. The water soluble salts of glyphosate are typically monobasic salts such as, for example, mono-isopropylamine, mono-potassium, or mono-ammonium salts or dibasic salts such as the diammonium salt. For many applications, a surfactant is incorporated into the glyphosate formulation to improve the herbicidal performance of the glyphosate salt. Unfortunately, however, many surfactants are not suitable for incorporation into formulations having a high glyphosate loading and may require relatively high surfactant loadings to provide sufficient impact on performance. The use of certain surfactants may also require the presence of other surfactants to improve the compatibility of the surfactant, and/or the performance of the formulation, and/or ameliorate problems in handling the formulations.

Aqueous concentrates comprising ammonium glyphosate salts are preferred for many applications because ammonia is relatively inexpensive and functions as a nutrient for vegetation, not as an environmental contaminant. On the other hand, ammonium salts tend to present compatibility problems, i.e., ammonium glyphosate concentrates are generally more susceptible to phase separation than other glyphosate salts such as the isopropylamine ("IPA") salt. As a consequence, ammonium glyphosate has typically been formulated with surfactants in either solid form or in aqueous concentrates more dilute than the IPA salt formulations that were the standard of the industry for many years.

File
150

Ammonium glyphosate salts are more compatible with quaternary ammonium salt surfactant than with other cationic surfactants. However, it has proved difficult to exploit this unique compatibility in the form of high strength ammonium glyphosate concentrates because of the relatively acute eye toxicity of most quaternary ammonium salts. To provide high load ammonium glyphosate concentrates which can be diluted to produce tank mixes comprising herbicidally effective ratios of surfactant to glyphosate, it has been deemed necessary to incorporate the quaternary ammonium surfactants into the concentrate at levels which have a relatively severe lachrimating effect. Conventionally, polyalkylene oxide alkyl ether surfactants have been used to limit eye toxicity of glyphosate salt concentrates comprising alkoxylated quaternary alkylammonium salt surfactants, while alkylene glycols and alkylene ether glycols are typically present in glyphosate concentrates that comprise alkoxylated quaternary alkylammonium salt and polyoxyethylene oxide alkyl ether surfactants. While effective against eye toxicity, nonionic surfactants such as polyalkylene oxide alkyl ethers can compromise the stability of high load ammonium glyphosate concentrates containing relatively high concentrations of alkoxylated quaternary alkylammonium salt surfactants, i.e., the stability gained by use of an alkoxylated quaternary alkyl ammonium surfactant is at least partially lost due to the destabilizing effect of the nonionic surfactant incorporated to control eye toxicity. Thus, those skilled in the art are confronted with a dilemma (or a tetralemma) i.e., whether to: (i) sacrifice glyphosate loading in favor of (stability + low eye irritancy + efficacy); (ii) sacrifice the efficacy provided by alkoxylated quaternary alkylammonium salt surfactants for (high glyphosate loading + stability + low eye irritancy); (iii) sacrifice stability in favor of (high glyphosate loading + efficacy + low eye irritancy); or (iv)

780
151

ACA6355WO (MTC 6920.8)
PCT

6

sacrifice desirable handling properties in favor of (glyphosate loading + stability + efficacy) by accepting relatively severe eye toxicity.

The Present Invention

In accordance with the invention, Applicant has discovered stable high load ammonium glyphosate concentrates which contain efficacious concentrations of alkoxylated quaternary alkylammonium salt surfactants and exhibit low eye toxicity, but which can be formulated with minimal concentrations of polyalkylene oxide alkyl ethers or other nonionic surfactants. It has further been found that the concentrates can be formulated with minimal concentrations of alkylene glycols, minimal concentrations of alkylene ether glycols, and/or with minimal concentrations of either nonionic surfactants, alkylene glycols, or alkylene ether glycols. Certain preferred formulations may be substantially devoid of each, any, and/or all of these. The absence or substantial absence of polyalkylene oxide alkyl ethers and other nonionic surfactants in the formulations of the present invention contributes to their stability.

Prior to the present invention, it had been understood that, to meet the eye toxicity standards of at least some jurisdictions without incorporating a significant fraction of nonionic surfactant, the concentrations of quaternary ammonium salt surfactants in ammonium glyphosate concentrates must be maintained at levels significantly lower than those desired for herbicidal efficacy. However, in accordance with the invention, it has been found that low eye toxicity can be preserved at surfactant concentrations that provide suitable herbicidal efficacy, for example, where the ratio of glyphosate, a.e., to the sum of alkoxylated quaternary alkylammonium salt(s) is between about 3 and about 20, as

defined in claim 37, or between about 3 and about 10, as defined in claim 38.

A. Novelty of claims 15-87 over D2

U.S. Patent No. 5,998,332 (D2) describes ammonium glyphosate formulations, preferably including a cationic surfactant such as a quaternary alkylammonium salt (e.g., methyl bis(2-hydroxyethyl)coco ammonium chloride). The invention of D2 is described as the discovery that surfactant compatibility improves with increasing mole ratio of ammonia to glyphosate, including ammonia to glyphosate molar ratios in excess of 1 or, more preferably, in excess of 1.5 (e.g., from about 1.6 to about 2.0 or from about 1.8 to about 1.95).

The working examples of D2 describe herbicidal formulations prepared by mixing one of Solutions 1, 2, and 3 containing glyphosate with one of Surfactant Mixtures A, B, and C. The latter Mixtures contain a quaternary surfactant (methyl bis(2-hydroxyethyl)coco ammonium chloride), a polyoxyethylene alkyl ether (polyoxyethylene secondary C₁₂₋₂₃ alkanol), diethylene glycol, and water in varying proportions. Mixtures A and B contain the quaternary surfactant and polyoxyethylene alkyl ether at weight ratios of about 4.3:1 and about 4.4:1, respectively. Mixture C is described as containing from 40-44% quaternary ammonium surfactant and from 9-10% polyoxyethylene alkyl ether; thus, the weight ratio of these components may not be definitively calculated. Attributing to Mixture C the averages of the stated ranges for the concentrations of components yields a weight ratio of quaternary surfactant to polyoxyethylene alkyl ether of approximately 4.42:1. However, based on the variability of these components expressed in this Mixture, the express teaching of D2 cannot be construed as definitively teaching a 4.42:1 ratio, or any other specific ratio calculated from a

152
153

ACA6355WO (MTC 6920.8)
PCT

8

combination of values falling within the combination of stated ranges.

Accordingly, D2 fails to teach any quaternary salt to polyoxyalkylene oxide alkyl ether ratio greater than 4.5:1 as called for in claim 15. Claim 17 further distinguishes D2 by calling for a ratio of alkoxyated quaternary alkylammonium salt surfactant to polyoxyalkylene oxide alkyl ether surfactant greater than about 5.2:1. Even if the upper end of the disclosed range for quaternary ammonium surfactant of Mixture C were coupled with the lower end of the range disclosed for polyoxyethylene surfactant, the calculated ratio would be no more than about 4.9:1, well below the ratio of greater than about 5.2:1 called for in claim 17. Thus, D2 generally exemplifies combinations of quaternary ammonium surfactants and relatively substantial fractions of additional nonionic surfactants (i.e., the polyoxyethylene alkyl ether diethylene glycol included in Mixtures A, B, and C). This reference includes no express teaching to exclude or limit the proportion of either polyalkylene oxide alkyl ether or any other nonionic surfactants, as is required by applicant's claim 15 and various claims depending therefrom. Accordingly, applicant respectfully submits independent claim 15 (original claim 23) and claims 16 to 42 and 46 to 76 depending therefrom are novel over the disclosure of D2.

The generic disclosure of D2 describes a variety of suitable surfactants including quaternized long chain amines, quaternized polyalkylene long chain amines (e.g., methyl bis(2-hydroxyethyl)coco ammonium chloride), quaternized pyridines, quaternized carboxylated imidazolines, trialkylbetaines, and amine oxides (e.g., di(hydroxyethyl)tallowamine oxide). The only quaternary surfactant utilized in the working examples of D2 is methyl bis(2-hydroxyethyl)coco ammonium chloride present in Surfactant Mixtures A, B, and C.

153
154

Thus, D2 includes no disclosure of quaternized surfactants derived from tallowamine. Accordingly, applicant respectfully submits that independent claim 43 (original claim 51) and dependent claims 44 and 45 are novel over the disclosure of D2 on the basis of requiring the presence of at least one alkoxyated quaternary alkylammonium salt surfactant predominantly comprising an N-alkyl substituent derived from tallow. As described in applicant's specification and known to those skilled in the art, surfactants derived from tallowamine are lower in cost and more efficacious on broadleaf weeds than surfactants derived from cocoamine. Accordingly, the efficacious herbicidal formulations of the present invention that exhibit low eye toxicity and incorporate surfactants derived from tallow represent a significant advance over the prior art.

Likewise, applicant respectfully submits new claims 77 to 87 are novel over the disclosure of D2. Independent claim 77 requires a degree of alkoxylation between about 3 and about 10 whereas the only alkoxyated quaternary alkylammonium salt surfactant utilized in the Mixtures of D2 contains an average value of only 2 ethylene oxide units. Independent claim 81 requires the presence of at least two quaternary ammonium surfactants, a feature also not taught in the examples of D2. Even if the generic disclosure of D2 were construed as describing the inclusion of two quaternary ammonium surfactants, there is no disclosure of incorporating any surfactant substituted with an average of 5 to 15 alkylene oxide units as specified in claim 81.

B. Novelty of claims 15-87 over D1

WO 94/02021 (D1) describes glyphosate-containing herbicidal formulations including quaternary ammonium compounds, as defined in the formula detailed therein. D1 generically discloses a list of glyphosate salts suitable for

757
155

use in formulations that includes ammonium salts. (See, page 4, lines 35-37) However, this passage also expresses a clear preference for the isopropylamine salt of glyphosate and the working examples of D1 are limited exclusively to formulations including the monoisopropylamine salt.

Although D1 routinely includes ammonium glyphosate in a list of the various glyphosate salts that may be used as herbicides, the reference contains no disclosure of any formulation containing ammonium glyphosate. In fact, the only formulations actually disclosed contain the isopropylamine salt, which has been the predominant commercial source of glyphosate over the past 25 years.

As described in the Sato patent (D2) and/or applicant's specification, constraints are encountered in formulating ammonium glyphosate salts and cationic surfactants. These include incompatibility of surfactants with the ammonium salt, instability of ammonium salt formulations generally, and eye toxicity of ammonium glyphosate formulations containing quaternary ammonium salt surfactants. D1 recognizes eye toxicity as a problem with glyphosate formulations generally, but fails to acknowledge the dilemma respecting the inclusion or exclusion of nonionic surfactants, especially in the case of ammonium glyphosate formulations containing cationic surfactants. The reference fails to recognize either the beneficial effect of nonionics on eye toxicity of formulations containing ammonium glyphosate and a quaternary ammonium salt surfactant, or the negative effect of nonionics on the stability of such formulations.

In fact, the teachings of D1 refer to glycols as "solubilizing agents," thus entirely missing the negative effect of glycol ether surfactants on formulation stability. While the generic disclosure of D1 also states that "no additional solubilizing agent such as a glycol is necessary to prevent the surfactant from gelling when added to water," this

158
156

representation should be read in the context of a specification where the only exemplary disclosure is of concentrates wherein the glyphosate source is exclusively the IPA salt. Moreover, the specification goes on to acknowledge that ingredients other than a glyphosate salt and ethoxylated quaternary alkylammonium salt surfactant can nevertheless be present. Specifically, the text recognizes that the formulation can contain any of various nonionic surfactants such as the ethoxylated alcohols. Significantly, these nonionics are also used in the exemplary ammonium glyphosate formulations of D2. In its generic disclosure, D1 lists still other ingredients that may be present in the formulation, including ammonium sulfate and/or polyethylene glycols such as PEG-400. D1 discloses no upper limit on the concentration of any such components. Moreover, it reflects neither recognition of the problems that can be created by nonionics nor any admonition that the concentrations thereof be limited.

More particularly, there is no suggestion in D1 that the ratio of alkoxyated quaternary alkylammonium salt surfactant to polyalkylene oxide alkyl ether surfactant in an ammonium glyphosate concentrate be at least about 4.5:1 as specified in instant claim 15. Nor is there any remote suggestion in D1 that the ammonium ion to glyphosate ratio be maintained between about 0.8 and about 2.5 as further required by claim 15, or 0.75 to 2.5 as called for by claims 77-87. As noted, D1 discloses that the glyphosate salt formulation may optionally contain ammonium sulfate. As indicated by the working examples of the Sato patent (D2), formulations containing ammonium glyphosate and an alkoxyated quaternary alkylammonium salt surfactant may often include a substantial proportion of ammonium sulfate. Where ammonium sulfate is included in such a formulation, the ammonium ion to glyphosate ratio is typically well in excess of 2.5, the maximum permitted by any of claims 15-87.

Although the D1 working examples do not include nonionic surfactants or ammonium sulfate, these examples are limited to formulations of the isopropylamine salt of glyphosate. As those skilled in the art are aware, the isopropylamine salt is generally more forgiving than the ammonium salt with respect to both the need for and penalties of nonionic surfactants. Thus, the D1 working examples have little or nothing to tell those skilled in the art about the problem of formulating ammonium glyphosate salts with alkoxylated quaternary alkylammonium salt surfactants, or with any other surfactant.

In view of these considerations, it is respectfully submitted that claims 15-87 are novel over the disclosure of D1 on the basis of requiring the presence of an ammonium salt of glyphosate and/or a weight ratio of quaternary surfactants to any polyalkylene oxide alkyl ether surfactant(s) of greater than 4.5:1 and/or the specified ammonium ion to glyphosate ratio of about 0.8 to about 2.5 (claims 15-76) or about 0.75 to about 2.5 (claims 77-87).

Applicants further respectfully submit that claims 43-45 and 77-87 are novel over the disclosure of D1 on the basis of additional limitations present therein. Claim 43 requires that at least one quaternary ammonium surfactant comprises an N-alkyl substituent derived from tallow. D1 generically discloses ammonium salts of glyphosate and separately discloses that surfactants used in glyphosate formulations may be derived from tallowamine, but does not disclose or suggest the particular combination of ammonium glyphosate and alkoxylated quaternary alkylamine derived from tallow. The working examples of D1 entirely fail to suggest such combination. They describe only isopropylamine salts of glyphosate in combination with alkoxylated quaternary salt surfactants derived from coconut oil.

Nothing in D1 suggests a formulation having a degree of alkoxylation between about 3 and about 10 as called for in claim 77. The quaternary ammonium salt surfactant utilized in Examples 1-3 of D1 is substituted with an average of 15 moles of ethylene oxide per mole of amine and the remaining disclosure of D1 is equally deficient so far as the claimed degree of alkoxylation is concerned. The examples of D1 likewise fail to include a formulation including two quaternary ammonium surfactants as required in claim 81. Even if incorporating two quaternary ammonium surfactants were attributed to the disclosure of D1, there is no disclosure of incorporating two such surfactants having the degrees of alkoxylation specified in claim 81.

C. Inventive Step of claims 15-87 over D2 and D1

The present invention confronts the problem of providing a stable ammonium glyphosate formulation of relatively high glyphosate loading that contains an alkoxyated quaternary alkylammonium salt surfactant at an efficacious concentration, while avoiding the problems typically associated with high concentrations of such surfactant (e.g., eye toxicity). The closest identified prior art is D2, which does not either recognize the problem or offer applicant's claimed solution.

The solution to the problem, as defined in claims 15-87, is to provide an ammonium glyphosate formulation wherein the combination of glyphosate loading, ammonium ion concentration and selection of alkoxyated quaternary alkylammonium salt surfactant are such as to achieve desirable efficacy while effectively controlling eye toxicity in the entire absence of polyalkylene oxide alkyl ether surfactants, or in which the polyalkylene oxide alkyl ether concentration is controlled at a level which has the least adverse effect on stability of the formulation. In the solution to the problem as defined in claim 15, the weight ratio of the sum of all alkoxyated alkyl

LS
159

quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) present in the formulation of greater than 4.5:1.

Whether taken alone or in combination, D1 and D2 fail to place the person of ordinary skill in the art in possession of the problem solutions defined in claims 15-87. While these references describe herbicidal formulations containing quaternary ammonium surfactants, they fail to disclose formulations exhibiting the features of the formulations defined in these claims.

D2 recognizes that, due to the compatibility problems associated with ammonium glyphosate and cationic surfactants, the object of achieving a high ammonium glyphosate loading conflicts with the object of providing an herbicidally efficacious concentration of an alkoxylated quaternary alkylammonium salt surfactant. D2 focuses on the surprising discovery that compatibility with cationic surfactants increases with increasing molar ratio of ammonium ion to glyphosate, and the claims of D2 all call for the formulation to have a pH between about 6 and about 7.

D2 also describes and exemplifies incorporation of nonionic surfactants into the formulation. Nonionics have the capability of reducing the eye toxicity of ammonium glyphosate formulations, but this is not mentioned in the reference. D2 does not address the eye toxicity problem. Nor does it recognize that the stability of a formulation containing ammonium glyphosate and an alkoxylated quaternary alkylammonium salt surfactant can be compromised by the presence of significant fractions of nonionic surfactants generally or polyalkylene oxide ether surfactants in particular.

Thus, D2 provides no teaching or allusion as to any of the solutions detailed in the pending claims. More particularly, D2 fails to suggest that efficacious and stable

formulations exhibiting improved properties (e.g., low eye toxicity) can be prepared utilizing relatively high proportions of quaternary ammonium surfactants in the absence or substantial absence of polyalkylene oxide alkyl ethers or other additional surfactants, thereby avoiding disadvantages associated with the presence of additional surfactants such as reduced stability. As noted above, in the exemplary disclosure of D2 weight ratios of the sum of all alkoxyated alkyl quaternary ammonium salt surfactant(s) to polyalkylene oxide alkyl ether surfactant(s) fall outside the prescribed range of claim 15. D2 attributes no significance to this ratio, and offers no reason why the ratio of alkoxyated quaternary alkylammonium salt to polyalkylene oxide alkyl ether should be above rather than below the ratios embodied in its working examples. Much less does it offer any teaching or suggestion of the combination of the instantly claimed ratio of ≥ 4.5 with the other elements of claim 15, including the claimed ratio of ammonium ion to glyphosate which excludes the examples of D2 that contain ammonium sulfate. D2 not only fails to offer any solution to the problem confronted by Applicant, but fails even to recognize the existence of the problem. Only through impermissible hindsight in view of applicant's disclosure could one skilled in the art view D2 as teaching the claimed formulation. Unless armed with the disclosure of applicant's specification, one skilled in the art would not have been placed in possession of applicant's invention, since D2 does not mention either eliminating or minimizing polyalkylene oxide alkyl ether surfactants.

As noted, D2 also fails to disclose alkoxyated quaternary alkylammonium salts that include an N-alkyl substituent derived from tallow, as required in claims 43 to 45. The invention of these claims addresses the problem of providing stable ammonium glyphosate concentrates of high efficacy and low cost. As discussed above, alkoxyated

160
161

ACA6355WO (MTC 6920.8)
PCT

16

quaternary alkyl ammonium salts derived from tallowamines afford higher efficacy at lower cost than those based on cocoamine. Formulations as defined in claim 71 achieve these advantages in stable high load formulations.

Furthermore, D2 does not disclose that the degree of alkoxylation of the quaternary ammonium surfactant should be controlled or varied as required in claims 77 and 81. Applicant respectfully submits that there is no teaching in D2 which either solves or recognizes the problem dealt with by the present invention. With respect to these claims also, only the hindsight afforded by Applicant's specification could have led those skilled in the art to the combinations which the claims define.

D1 generically discloses ammonium salts in a routine list of glyphosate salts, but exemplifies only the monoisopropylamine salt, and suggests no purpose for minimizing or excluding polyalkylene oxide alkyl ethers or other nonionic surfactants. D1 includes no teaching or suggestion of the desirability of formulations comprising either: (i) a weight ratio of quaternary surfactants to any polyalkylene oxide alkyl ether surfactant(s) of greater than 4.5:1 as required in claim 15; or (ii) a quaternary ammonium surfactant comprising a component derived from tallowamine as called for in claim 43; or (iii) surfactant(s) exhibiting the degree of alkoxylation specified in independent claims 77 and 81. Thus, D1 also fails to either identify or offer any solution to the problem with which the instant invention contends. Even the acumen of hindsight would be strained to find the elements of the claimed formulations in the teachings of D1, D2 or any combination of these references.

Based on the foregoing, applicant respectfully submits claims 15-87 involve an inventive step over D2 and D1.

162

II. Claims 1-22

In accordance with the instant amendment, the subject matter of original claims 1-22 is now presented with appropriate amendments in claims 1-14.

Claim 1

Independent claim 1, as amended, is directed to a stable herbicidal formulation that comprises a glyphosate salt at a concentration in the range of 300-600 g a.e./l and a surfactant adjuvant that comprises at least one alkoxyated quaternary ammonium cationic surfactant. The formulation of claim 1, as amended, contains less than about 0.1% by weight polyoxyethylene alkyl ethers and the ratio of glyphosate (wt% a.e.) to the alkoxyated quaternary ammonium cationic surfactant is between 10:1 to 30:1.

A. Novelty and Inventive Step of claims 1-14 over D1 and D2

The formulation of claim 1 addresses the problem of providing stable ammonium glyphosate concentrates which contain an alkoxyated quaternary alkylammonium salt surfactant yet exhibit acceptable eye toxicity. The solution to the problem comprises the claimed combination of components wherein a polyalkylene oxide alkyl ether concentration less than about 0.1 weight % contributes to stability, while the claimed ratio of glyphosate to alkoxyated quaternary alkylammonium salt contributes to both stability and low eye toxicity.

As noted, D1 and D2 each disclose quaternary ammonium surfactants and/or herbicidal formulations containing such surfactants, but neither reference discloses a quaternary ammonium surfactant-containing herbicidal formulation as defined in amended claim 1.

163

D1 describes glyphosate-containing herbicidal formulations including alkoxylated quaternary alkylammonium compounds, as defined in the formula detailed therein, in which the weight ratio of surfactant to glyphosate is between about 1:5 and about 5:1. While the reference generically lists ammonium glyphosate salts in a list of conventional salts, the entire disclosure including the working examples is directed to isopropylamine salts. In particular, the working examples of D1 describe isopropylamine/glyphosate formulations including a polyoxyethylene quaternary alkyl methyl ammonium chloride derived from coconut oil having average of 15 EO/amine (ETHOQUAD C/25) and a "small amount" of PEG-400. Examples 1, 2, and 3 include isopropylamine/glyphosate and the quaternary surfactant at relatively low weight ratios of glyphosate (wt.% a.e.) to surfactant, i.e., 1.63, 1.77, and 2.81, respectively. These are far below the range of glyphosate to quaternary surfactant specified in claim 1.

The working examples of D2 describe herbicidal formulations containing glyphosate at concentrations ranging from 470 g a.e./l (Example 1) to 540 g a.e./l (Example 4). As noted, these formulations contain one of Surfactant Mixtures A, B, and C. Each of Mixtures A, B and C includes a quaternary surfactant, methyl bis(2-hydroxyethyl)coco ammonium chloride. The weight ratios of glyphosate (a.e.) to quaternary ammonium surfactant for the examples of D2 vary widely, from about 7.7:1 to about 62.5:1, thus overlapping but not teaching the instantly claimed range of 10:1 to 30:1. None of the D2 examples fall within this range. The concentrations of polyoxyethylene alkyl ether in the formulations of the working examples of D2 range from 0.19 wt% to 1.5 wt%, distinctly above the 0.1 wt.% maximum permitted by claim 1.

Applicant respectfully submits that neither D1 nor D2 disclose an herbicidal formulation as defined in claim 1.

Neither reference discloses an herbicidal formulation that includes a quaternary ammonium surfactant in a concentration less than about 0.1% by weight polyoxyethylene alkyl ethers and contains glyphosate in a weight ratio to alkoxyated quaternary alkylammonium salt between 10:1 and 30:1. Moreover, neither of these references includes any disclosure of the desirability of modifying either or both of these features to arrive at the invention defined in claims 1-14. Thus, no reasonable combination of these references can be viewed as solving the problem dealt with by Applicant's novel formulation. Only through hindsight in view of applicant's disclosure could one skilled in the art be apprised of the suitability of such a combination. Accordingly, applicant respectfully submits claims 1-14 are both novel and inventive over the disclosures of D2 and D1.

B. Novelty and Inventive Step of claims 1-14 over D3-D10

Other references cited against claim 1 describe herbicidal formulations including quaternary ammonium surfactants. However, these references also fail to either disclose the herbicidal formulations defined in claims 1-14 or otherwise place one of skill in the art in possession of the invention defined in claims 1-14. It is therefore submitted that these claims are both novel and inventive over these references as well.

Laerke & Streibig (D7) describes an investigation of the effect on glyphosate formulations of various surfactants, including a quaternary ammonium surfactant (Trimao). Each surfactant was tested in varying concentrations (of 0.27, 1.35, 2.71, and 5.42 g/l) in combination with glyphosate monoammonium salt at concentrations of 0.07, 1.35, 2.71, and 4.06 g a.e./l. Thus, D7 discloses only so-called "tank mixes," i.e. aqueous glyphosate compositions diluted to the

165

ACA6355WO (MTC 6920.8)
PCT

20

strength at which they are applied to vegetation. Tank mixes do not present stability or eye toxicity problems comparable to those of glyphosate concentrates. However, tank mixes are not suitable for shipping and storage because of their high weight and volume per unit weight of glyphosate. Concentrated formulations are developed to facilitate shipping and storage, but the high glyphosate content of such formulations, e.g., 300 to 600 g/L a.e. as specified in claim 1, and proportionately high surfactant content, raise the stability and eye toxicity concerns with which the present invention deals. For these reasons, one skilled in the art would not rely on the ratios of glyphosate to other components in a tank mix as being suitable in a concentrate. More particularly, one skilled in the art would know that ratios of surfactants to glyphosate which are benign in a tank mix can lead to serious stability, eye toxicity or other problems in a concentrate containing glyphosate in a concentration of 300+ g/L a.e. Therefore, D7 has essentially no relevance to the formulation of claim 1, and certainly does not affect the novelty thereof.

The remaining cited references fail to disclose or suggest utilizing glyphosate to quaternary surfactant ratios as prescribed in claim 1 and also fail to disclose or suggest minimizing the presence of polyoxyethylene alkyl ethers as prescribed in claims 1-14. Thus, applicant respectfully submits that the invention defined in claims 1-14 is novel and involves an inventive step over the disclosures of each of these references.

For example, EP 0 582 561 (D3) discloses a water-soluble granular composition prepared by extrusion that comprises N-phosphonomethylglycine or a salt thereof, a surfactant, and an extrusion aid. The working examples of D3 describe formulations including monoammonium glyphosate, a cationic surfactant (e.g., Ethoquad 18/25), and a processing aid such

as polyethylene glycol. However, the working examples of D3 fail to disclose an herbicidal formulation as defined in claim 1. The calculated glyphosate to quaternary ammonium surfactant weight ratios for the working examples of D3 range from about 4.5:1 to about 7.6:1, well below the starting point for the range required in claim 1, as amended.

EP 0 274 339 (D4) discloses glyphosate formulations including quaternary ammonium surfactants (e.g., methyl bis(2-hydroxyethyl)coco ammonium chloride), but does not disclose a formulation as defined in claim 1. In particular, the formulations of D4 described in Examples 1 and 3 exemplify weight ratios of glyphosate (wt. a.e.) to surfactant of 4.4:1 and 3.2:1, respectively.

Applicant respectfully submits claim 1 as amended is entitled to a priority date of September 23, 2004. In any event, claim 1 as amended is submitted as novel over the disclosure of D5. WO 2005/016002 (D5) discloses herbicidal formulations including glyphosate and a quaternary ammonium compound (e.g., Ethoquad C/12 listed in Table 1), but exemplifies a weight ratio of glyphosate (wt. & a.e.) to surfactant of 3.6:1 in Example 1, clearly outside the range prescribed in claim 1.

Wyrill & Burnside, 1977 (D6) generally describes an investigation of the effect of various surfactants on glyphosate toxicity to common milkweed and hemp dogbane, including quaternary ammonium salts. In particular, D6 describes incorporation of Ethoquad 18/12 and 18/25 surfactants into glyphosate formulations. However, as with D4 and D5, this reference fails to disclose an herbicidal formulation as defined in claim 1. Specifically, D6 fails to disclose a formulation comprising ammonium glyphosate and the quaternary ammonium surfactant at the prescribed weight ratio.

EP 0 526 444 (D8), U.S. Patent No. 5,462,912 (D9), and U.S. Patent No. 5,948,421 (D10) disclose herbicidal

167

ACA6355WO (MTC 6920.8)
PCT

22

formulations including glyphosate and a quaternary ammonium surfactant, but do not disclose a formulation as defined in claim 1. D9 does not disclose information from which the weight ratio of glyphosate (a.e.) to quaternary ammonium surfactant can even be calculated, while claim 4 of D8 calls for a weight ratio of glyphosate to quaternary ammonium surfactant of from 1:2 to 4:1. The weight ratios of glyphosate to quaternary ammonium surfactant exemplified in D10, 5.3:1 to about 8.5:1, fall entirely outside the prescribed range of claim 1.

Item VI (Certain documents cited)

Applicant respectfully submits subject matter of the present application properly claims a priority date of September 23, 2004. In any event, as noted above, the subject matter of claim 1, as amended, and claims 2-14 depending therefrom, is submitted as novel and inventive over the disclosure of D5.

Items VII and VIII

Article 6 PCT contains no limitation on the number of claims that can be presented in an application. It is further respectfully submitted that the present mix of claims, particularly the mix of independent claims, is necessary to protect the subject matter of the present invention. Thus, claims that are individually clear and concise cannot become otherwise simply because of their number, especially where the mix of claims is necessary to protect the underlying invention from being unfairly appropriated by competitors who have the benefit of applicant's disclosure in the subject application.

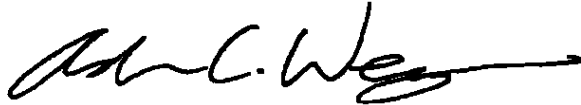
In view of the foregoing, favorable consideration and issuance of a favorable Examination Report for claims 1-87 are respectfully requested. If the Examiner has any further objections, it is respectfully requested that applicant be

ACA6355WO (MTC 6920.8)
PCT

23

given an opportunity to submit amendments or arguments before
the Examination Report is established (see Rule 66.4(b) PCT).

Respectfully submitted,



Andrew C. Wegman, Reg. No. 54,530
SENNIGER POWERS
One Metropolitan Square, 16th Floor
St. Louis, Missouri 63102
(314) 231-5400

ACW/lrw/JKR/caa/dlg
Mail Stop PCT
Express Mail Label No. EV 654633223 US

~~168~~
168

REPLACEMENT PAGE

What is claimed is:

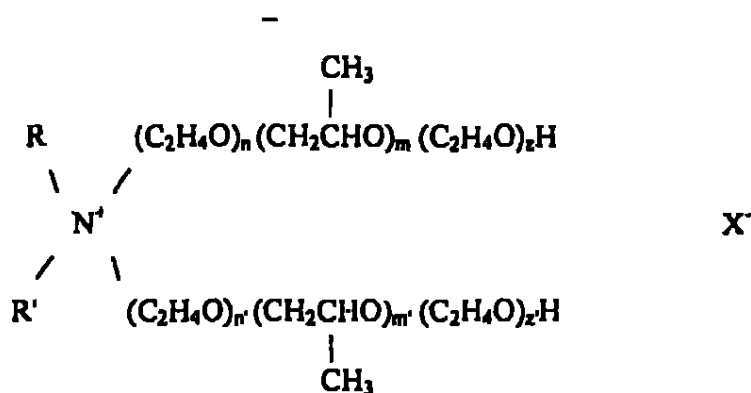
1. A stable, herbicidal formulation that comprises a glyphosate salt at a concentration in the range of 360-600 g a.e./l and a surfactant adjuvant, wherein said surfactant adjuvant comprises at least one alkoxyated quaternary ammonium cationic surfactant, the formulation contains less than about 0.1% by weight polyoxyethylenc alkylethers, and the ratio of glyphosate (wt% a.e.) to the alkoxyated quaternary ammonium cationic surfactant is between 10:1 to 30:1.
2. The formulation of claim 1 wherein said formulation contains no substantial amounts of other surfactants.
3. The formulation of claim 1 wherein said formulation is stable between -20 and 60°C, preferably -10 to 50°C and more preferably 0 and 40°C.
4. The formulation of claim 1 which additionally comprises at least one process aid.
5. The formulation of claim 4 wherein said process aid is a glycol.
6. The formulation of claim 1 wherein said alkoxyated quaternary compound is methyl bis(2-hydroxyethyl)coco ammonium chloride.
7. The formulation of claim 1 wherein the glyphosate salt is selected from the group sodium, potassium, ammonium, isopropylamine, monoethanolamine, diethanolamine, triethanolamine, trimethylsulfonium, and mixtures thereof.
8. The formulation of claim 7 wherein the glyphosate formulation is a stable liquid formulation with a concentration of glyphosate in the range of 450 – 580 g a.e./l.
9. The formulation of claim 1 which additionally comprises a co-herbicide.
10. The formulation of claim 9 wherein said co-herbicide is selected from the group consisting essentially of sulfonylurea, acifluorfen, asulam, benazolin, bentazon,

170

REPLACEMENT PAGE

bialaphos, bromacil, bromoxynil, chloramben, clopyralid, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, diquat, endothall, fenac, fenoxaprop, flamprop, fluazifop, fluoroglycofen, fomesafen, fosamine, glufosinate, haloxyfop, imazameth, imazamethabenz, imazamox, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naphtalam, nonanoic acid, paraquat, picloram, sulfamic acid, 2,3,6-TBA, TCA, triclopyr, salts thereof, and mixtures thereof.

11. The formulation of claim 1 wherein said alkoxyated quaternary ammonium compound is of General Formula I, below:



wherein R is a straight or branched chain, saturated or unsaturated alkylene group having from 8 to 22 carbon atoms; R' is a straight or branched chain, saturated or unsaturated alkylene group having from 1 to 4 carbon atoms; and n+n' is an integer of from 0-30, m + m' is an integer of from 0 to 30, and z + z' is an integer of from 0-30, with the proviso that n + z is at least 1 and/or n' + z' is at least 0 or 1, and X⁻ is an agriculturally compatible anion.

12. The formulation of claim 11 wherein said alkoxyated quaternary ammonium compound is methyl bis(2-hydroxyethyl)coco ammonium chloride.

13. The formulation of claim 12 wherein said formulation is a solid.

14. The formulation of claim 1 further comprising a herbicidally active compound is selected from the group consisting essentially of sulfonylurea, acifluorfen, asulam, bcnazolin, bentazon, bialaphos, bromacil, bromoxynil, chloramben, clopyralid, 2,4-D,

REPLACEMENT PAGE

2,4-DB, dalapon, dicamba, dichlorprop, diclofop, diquat, endosulf, fenac, fenoxaprop, flumetralin, fluroxypyr, fluoroglycofen, fomesafen, fosamin, glufosinate, haloxyfop, imazameth, imazamethabenz, imazamox, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naptalam, nonanoic acid, paraquat, picloram, sulfamic acid, 2,3,6-TBA, TCA, triclopyr, salts thereof, and mixtures thereof.

15. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 240 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.8 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula:



where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ and B is $(R^5O)_{p'}(R^6O)_{q'}(R^7O)_{z'}R^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, each of R^8 and R^9 is selected from the group consisting of hydrogen, methyl and ethyl, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $p + p' + q + q' + z + z'$ is at least about 2,

the weight ratio of the sum of all said alkoxyated alkyl quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) being greater than 4.5:1.

16. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 4.5:1.

17. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 5.2:1.

REPLACEMENT PAGE

18. A stable aqueous liquid herbicidal concentrate as set forth in claim 17 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 5.2:1.

19. A stable aqueous liquid herbicidal concentrate as set forth in claim 17 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 10:1.

20. A stable aqueous liquid herbicidal concentrate as set forth in claim 19 wherein the weight ratio of the sum of all said alkoxyated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 10:1.

21. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 comprising at least about 325 gpl glyphosate, a.e.

22. A stable aqueous liquid herbicidal concentrate as set forth in claim 21 comprising at least about 360 g/L glyphosate, a.e.

23. A stable aqueous liquid herbicidal concentrate as set forth in claim 22 comprising at least about 400 g/L glyphosate, a.e.

24. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 containing not more than about 5 wt.% ammonium sulfate.

25. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 3.25.

26. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the ratio of the sum of dialkoxyated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 4.

27. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein $(p + q + p' + q' + z + z') \geq 3$.

REPLACEMENT PAGE

28. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein said alkoxyated quaternary alkylamine surfactant(s) have a W_0 value between about 3 and about 20, where W_0 is the average value of $(p + p' + q + q' + z + z')$ for said surfactant(s).

29. A stable aqueous liquid herbicidal concentrate as set forth in claim 28 wherein the value of W_0 is between about 3 and about 7.

30. A stable aqueous liquid herbicidal concentrate as set forth in claim 28 wherein the value of W_0 is between about 6 and about 15.

31. A stable aqueous liquid herbicidal concentrate as set forth in claim 28 comprising a plurality of alkoxyated quaternary alkylammonium surfactants, the value of W_0 for at least one of said plurality of surfactants being about 2, and the value of W_0 for the other of said surfactants being in the range of between about 8 and about 15.

32. A stable aqueous liquid herbicidal concentrate as set forth in claim 31 wherein R of at least one of said plurality of alkoxyated quaternary alkylamine salt surfactants contains an average between about 16 and about 18 carbon atoms.

33. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein R of said alkoxyated quaternary alkylammonium salt surfactant(s) contains an average of between about 16 and about 18 carbon atoms.

34. A stable aqueous liquid herbicidal concentrate as set forth in claim 33 wherein R of said alkoxyated quaternary alkylamine salt surfactant is derived predominantly from tallow.

35. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the molar ratio of ammonium ions to glyphosate ions is at least about 1.2.

36. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the molar ratio of ammonium ions to glyphosate ions is at least about 1.5.

183
174

REPLACEMENT PAGE

37. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the weight ratio of glyphosate, a.e., to the sum of alkoxyated quaternary alkylammonium salt(s) is between about 3 and about 20.

38. A stable aqueous liquid herbicidal concentrate as set forth in claim 37 wherein the weight ratio of glyphosate, a.e., to the sum of alkoxyated quaternary alkylammonium salt(s) is between about 3 and about 10.

39. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the concentration of the sum of alkoxyated quaternary alkylammonium salt surfactant(s) is between about 3 wt.% and about 12 wt.%.

40. A stable aqueous liquid herbicidal concentrate as set forth in claim 39 wherein the concentration of the sum of alkoxyated quaternary alkylammonium salt surfactant(s) is between about 3.5 wt.% to about 10 wt.%.

41. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 having low eye toxicity.

42. A stable aqueous liquid herbicidal concentrate as set forth in claim 41 having a Red Band eye toxicity classification of yellow.

43. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 240 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.8 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant predominantly comprising an N-alkyl substituent derived from tallow.

44. A stable aqueous liquid concentrate as set forth in claim 43 wherein the weight ratio of the sum of all said alkoxyated alkyl quaternary ammonium salt surfactant(s) to any polyalkylene oxide alkyl ether surfactant(s) is greater than 4.5:1.

45. A stable aqueous liquid herbicidal concentrate as set forth in claim 43 comprising at least about 325 gpl glyphosate, a.e.

174
175

REPLACEMENT PAGE

46. The stable aqueous liquid herbicidal concentrate of claim 15 comprising an ammonium salt of glyphosate and containing greater than 38.0 wt.% /L glyphosate a.e., at least one alkoxylated quaternary alkylammonium salt surfactant wherein each of p, q, p' and q' is independently an integer between 0 and 3, said concentrate having a pH <7.3.

47. The stable aqueous liquid herbicidal concentrate of claim 46, said concentrate having an ammonia concentration over the solution that is less than about 750 ppm at 25°C.

48. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the weight ratio of the total of alkoxylated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and the molar concentration of alkoxylated quaternary alkylammonium ion in said aqueous concentrate being not greater than about 0.28.

49. A stable aqueous liquid concentrate as set forth in claim 48 wherein the molar concentration of said alkoxylated quaternary alkylammonium salt surfactant is not greater than about 0.25, 0.20, 0.15, 0.13, 0.10 or 0.08.

50. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 wherein R comprises between about 8 and about 18 carbon atoms.

51. A stable aqueous liquid herbicidal concentrate as set forth in claim 50 wherein R is predominantly derived from tallow.

52. A stable aqueous liquid herbicidal concentrate as set forth in claim 49 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 4.5:1.

53. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 5.2:1.

138
176

REPLACEMENT PAGE

54. A stable aqueous liquid herbicidal concentrate as set forth in claim 53 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 5.2:1.

55. A stable aqueous liquid herbicidal concentrate as set forth in claim 53 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any polyalkylene oxide alkyl ether surfactant(s) is greater than 10:1.

56. A stable aqueous liquid herbicidal concentrate as set forth in claim 55 wherein the weight ratio of the sum of all said alkoxylated quaternary alkylammonium salt surfactant(s) to the sum of any nonionic surfactant(s) is greater than 10:1.

57. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 comprising at least about 325 gpl glyphosate, a.e.

58. A stable aqueous liquid herbicidal concentrate as set forth in claim 57 comprising at least about 360 g/L glyphosate, a.e.

59. A stable aqueous liquid herbicidal concentrate as set forth in claim 58 comprising at least about 400 g/L glyphosate, a.e.

60. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 containing not more than about 5 wt.% ammonium sulfate.

61. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 wherein the ratio of the sum of dialkoxylated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 3.25.

62. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 wherein the ratio of the sum of dialkoxylated quaternary alkylammonium salt surfactant(s) to the sum of (alkylene glycol(s) + alkylene ether glycol(s)) is greater than about 4.

REPLACEMENT PAGE

63. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 having a Red Band eye toxicity classification of yellow.

64. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 wherein the molar concentration of alkoxylated quaternary alkylammonium ion is not greater than about 0.13.

65. A stable aqueous liquid herbicidal concentrate as set forth in claim 48 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

66. A stable aqueous liquid herbicidal concentrate as set forth in claim 15 wherein the weight ratio of the total of alkoxylated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and the number average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 2 and about 10.

67. The stable aqueous liquid herbicidal concentrate of claim 66 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 3 and about 10, or between about 3 and about 8, or between about 4 and about 8, or between about 5 and 10.

68. An aqueous liquid herbicidal concentrate as set forth in claim 66 wherein the molar concentration of alkoxylated quaternary alkylammonium ion is not greater than about 0.28, 0.25, or 0.20.

69. An aqueous liquid herbicidal concentrate as set forth in claim 66 wherein the molar concentration of alkoxylated quaternary alkylammonium ion is not greater than about 0.15.

70. A stable aqueous liquid herbicidal concentrate of claim 66 comprising at least two alkoxylated quaternary alkylammonium salt surfactants, wherein the average sum of $(p + p' + q + q' + z + z')$ for one of said at least two surfactants being between about 2 and about 5,

177
178

REPLACEMENT PAGE

and the average sum of $(p + p' + q + q' + z + z')$ for another of said at least two surfactants being between about 5 and about 15.

71. An aqueous liquid herbicidal concentrate as set forth in claim 70 wherein the weight ratio of the sum of said one and said another surfactants to ammonium glyphosate, a.e., being between about 0.1:1 and about 0.2:1.

72. An aqueous liquid herbicidal concentrate as set forth in claim 71 wherein the weight ratio of said one surfactant to said another surfactant is between about 1:1.5 and about 1.5:1.

73. An aqueous liquid herbicidal concentrate as set forth in claim 70 wherein the mole ratio of alkoxyated quaternary alkylammonium salt surfactant(s) to glyphosate is not greater than about 0.2:1.

74. An aqueous liquid herbicidal concentrate as set forth in claim 70 wherein the weight ratio of alkoxyated quaternary alkylammonium salt surfactant(s) to glyphosate is between about 0.1:1 and about 0.17:1.

75. An aqueous liquid herbicidal concentrate as set forth in claim 70 wherein the molar concentration of alkoxyated quaternary alkylammonium ion in said aqueous concentrate is not greater than about 0.15.

76. An aqueous liquid herbicidal concentrate as set forth in claim 70 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

77. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 120 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.75 and about 2.5, and at least one alkoxyated quaternary alkylammonium salt surfactant corresponding to the formula:



178
179

REPLACEMENT PAGE

where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ and B is $(R^5O)_p(R^6O)_q(R^7O)_zR^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $[p + p' + q + q' + z + z']$ is at least about 2,

the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.c., in said concentrate being between about 0.1:1 and about 0.2:1, and

the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 3 and about 10.

78. An aqueous liquid herbicidal concentrate as set forth in claim 77 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 3 and about 8.

79. An aqueous liquid herbicidal concentrate as set forth in claim 77 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 4 and about 8.

80. An aqueous liquid herbicidal concentrate as set forth in claim 77 wherein the average value of $(p + p' + q + q' + z + z')$ for said at least one surfactant is between about 5 and 10.

81. A stable aqueous liquid herbicidal concentrate comprising an ammonium salt of glyphosate and containing at least about 120 g/L glyphosate a.e., ammonium ion in a molar ratio to glyphosate between about 0.75 and about 2.5, and at least two alkoxyated quaternary alkylammonium salt surfactants corresponding to the formula:



REPLACEMENT PAGE

where R is a straight chain or branched chain, saturated or unsaturated alkyl group having from 8 to 22 carbon atoms, R' is a straight or branched chain, saturated or unsaturated alkyl group having from 1 to 4 carbon atoms, A is $(R^2O)_p(R^3O)_q(R^4O)_zR^8$ and B is $(R^5O)_p(R^6O)_q(R^7O)_zR^9$ where each of R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is independently selected from the group consisting of ethylene and isopropylene, and each of p, q, p', q', z and z' is independently an integer between 0 and 30 and the sum of $[p + p' + q + q' + z + z']$ is at least about 2,

the weight ratio of the total of alkoxyated quaternary alkylammonium surfactant(s) to ammonium glyphosate, a.e., in said concentrate being between about 0.1:1 and about 0.2:1, and

the average sum of $(p + p' + q + q' + z + z')$ for one of said at least two surfactants being between about 2 and about 5, and the average sum of $(p + p' + q + q' + z + z')$ for another of said at least two surfactants being between about 5 and about 15.

82. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the weight ratio of the sum of said one and said another surfactants to ammonium glyphosate, a.e., being between about 0.1:1 and about 0.2:1.

83. An aqueous liquid herbicidal concentrate as set forth in claim 82 wherein the weight ratio of said one surfactant to said another surfactant is between about 1:1.5 and about 1.5:1.

84. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the mole ratio of alkoxyated quaternary alkylammonium salt surfactant(s) to glyphosate is not greater than about 0.2:1.

85. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the weight ratio of alkoxyated quaternary alkylammonium salt surfactant(s) to glyphosate is between about 0.1:1 and about 0.17:1.

180
181

ACA6355WO (MTC 6920.8)
PCT

33

REPLACEMENT PAGE

86. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the molar concentration of alkoxylated quaternary alkylammonium ion in said aqueous concentrate is not greater than about 0.15.

87. An aqueous liquid herbicidal concentrate as set forth in claim 81 wherein the total molar concentration of all quaternary ammonium ions is not greater than about 0.15.

101
182

PCT MISCELLANEOUS

File ACA535540 (MIT 6920.8) Attorney AOW/dlg
Client Alzo Nobel NV
Inventor(s) Zhu et al.
Serial No. PCT/US2006/034076

The following has been received by the U.S. Patent and Trademark Office on the date stamped hereon:

☐ Signed PCT Request Form	☐ Notice of Withdrawal
☐ Notice of Confirmation of Precautionary Designations	☐ Chapter II Demand Form PCT/IPEA/401
☐ Check \$ _____	☐ Drawings (_____ sheets)
☐ Article 19 Amendment (re search report)	☒ Article 34 Amendment (re written opinion)
☐ Letter to Commissioner	☐ Fee Calculation Sheet
☒ Response to PCT Invitation	☐ Reprinted Application
☒ Certificate of Mailing by "Express Mail" No. <u>950463323US</u>	
☒ Replacement claim pages *	

RECEIVED SEP 18 2006

IAP15 Rec'd PCT/PTO 12 SEP 2006

183

PCT MISCELLANEOUS

File ACW/353d (MIC 6920.8) Attorney ACW/dlg
Client Alkzo Nobel NV
Inventor(s) Zhu et al.
Serial No. PCT/US2005/034076
The following has been received by the U.S. Patent and Trademark Office on the date stamped hereon:

☐ Signed PCT Request Form	☐ Notice of Withdrawal
☐ Notice of Confirmation of Precautionary Designations	☐ Chapter II Demand Form PCT/IPEA/401
☐ Check \$ _____	☐ Drawings (_____ sheets)
☐ Article 19 Amendment (re search report)	☒ Article 34 Amendment (re written opinion)
☐ Letter to Commissioner	☐ Fee Calculation Sheet
☒ Response to PCT Invitation	☐ Reprinted Application
☒ Certificate of Mailing by "Express Mail" No. <u>EV6463322-15</u>	
☒ Replacement claim pages	



EV 654633223 US

Mailing Label
Label 11-F, April 2004



UNITED STATES POSTAL SERVICE

Post Office To Addressee

ORIGIN (POSTAL SERVICE USE ONLY)				DELIVERY (POSTAL SERVICE USE ONLY)			
PS ZIP Code	Day of Delivery	Postage		Delivery Attempt	Time	Employee Signature	
	☐ Next ☐ First ☐ In/Del. Day	Return Receipt Fee		Mo. Day	☐ AM ☐ PM		
Date Accepted	Scheduled Date of Delivery	Insured Fee		Delivery Attempt	Time	Employee Signature	
Mo. Day Year	Month Day	COD Fee		Mo. Day	☐ AM ☐ PM		
Time Accepted ☐ AM ☐ PM	Scheduled Time of Delivery	Insured Fee		Delivery Date	Time	Employee Signature	
	☐ Mon ☐ Tue ☐ Wed ☐ Thu ☐ Fri ☐ Sat ☐ Sun	Total Postage & Fees		Mo. Day	☐ AM ☐ PM		
Flat Rate ☐ or Weight	Int'l Alpha Country Code	Acceptance Emp. Initials		☐ Signature for undelivered item(s) and only additional consideration required to reschedule delivery to alternate address without obtaining signature of addressee or addressee's agent. If delivery employee judges that notice can be left in care of addressee and it indicates that delivery employee's signature constitutes valid proof of delivery.			
FROM: PLAINFIELD NJ 07054				TO: (PLEASE PRINT)			
314 231 5400				MAIL STOP PCT			
SENNIGER POWERS				Commissioner for Patents			
1 METROPOLITAN SQ FL 16				P.O. Box 1450			
SAINT LOUIS MO 63102-2711				Alexandria, VA 22313-1450			
MIC 6920.8 +1 ACW/dlg				Response to Invitation to Submit Amendments with Article 34 Amendment and Amended Claims			

PRESS HARD. YOU ARE MAKING 3 COPIES.

171/500

F:02 T:

185

Apostille

(Convention de La Haye du 5 octobre 1961)

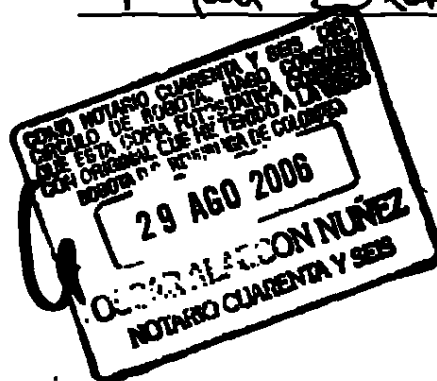
1. Country: United States of America

- This public document
2. has been signed by CAITLIN E. MACAGY
3. acting in the capacity of NOTARY PUBLIC
4. bears the seal/stamp of CAITLIN E. MACAGY-NOTARY PUBLIC-STATE OF MISSOURI

Certified

5. at Jefferson City, Missouri
6. the 28th. day of JANUARY, 2002
7. by Matt Blunt, Secretary of State, State of Missouri
8. No. 70695
9. Seal/Stamp
10. Signature:

Comm. 48 (12-2000)



PODER

POWER OF ATTORNEY

186

El abajo firmado

The undersigned MONSANTO TECHNOLOGY LLC, a Delaware Limited Liability company, located at 800 North Lindbergh Boulevard, St. Louis, Missouri, United States of America

Nombre por el presente a

hereby appoint Ramiro Castro-Duque y/o Juan Pablo Cadena Sarmiento y/o Beatriz Jaramillo S.

a los apoderados que él o ellos designen nuestro representante legal y verdadero en Bogotá, con facultades para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales, con el fin de dar cumplimiento al párrafo 1o, del Artículo 543 del Decreto 410 de 1971, quedando especialmente facultados para representarnos ante las autoridades Colombianas, administrativas, judiciales o de policía, en todos los trámites relativos a la Propiedad Industrial, a cuyo efecto les facultamos para dar ante dichas autoridades todos los pasos necesarios al objeto indicado; elevar solicitudes, declaraciones y reclamos; formular descripciones, enmiendas; oposiciones y apelaciones; instaurar cancelaciones; abonar todos los impuestos y cuotas y efectuar todo otro pago determinado por la ley; recibir todos los documentos y valores, dando el descargo respectivo; llenar cualesquiera otros requisitos y tomar, en fin, todas las medidas que creyen conducentes al resguardo de nuestros intereses; y en caso de producirse oposición, pasar los antecedentes a los tribunales, quedando facultado, para intervenir como demandante o demandado ante los jueces que sean competentes, pudiendo transar, someter a arbitros, desistir, percibir y apelar, con todas las demás facultades que resulten necesarias, y por el presente declaramos desde ahora válido y bueno cuanto dicho representante y/o los apoderados que el nombre hicieren en nuestro beneficio.

or the agents appointed by him or them, our true and legal representative in Bogota, with power to receive notifications and to appoint judicial or extrajudicial agents, so as to comply with paragraph 1, Article 543 of Decree 410 of 1971, and they are especially empowered to represent us before the administrative, judicial or police authorities of Colombia in all proceedings pertaining to industrial property, for which purpose we authorize them to take before the said authorities all the necessary steps to the said end; to file petitions, declarations, claims, cancellations, and administrative injunction proceedings; to draw up specifications; to make amendments, oppositions and appeals, to pay all installments and effect all other payments prescribed by law; to receive proper receipts, to comply with all other requirements and, in short, to take all those measures which may deem fit for the protection of our interests; and in case of opposition, where the proceedings be passed over to the courts, we authorize said agent(s) to act on our behalf, as complainant(s) as well as defendant(s), before the competent judges, with full powers to make arrangements, to submit to arbitrators, to desist, to collect, to appeal and, in short, with all such further powers as may be required; and we hereby declare from now on as valid and good all that said representative and/or the agents by him appointed may do for our benefit.

Asimismo, facultamos a los abogados arriba indicados para solicitar en la Oficina de Propiedad Industrial la protocolización de este documento y de cualquier poder que otorguen a nombre nuestro.

We also authorize said attorneys to apply for protocolization of this document and any power of attorney by him conferred in our name, before the Office of Industrial Property, as well as to substitute these presents.

Given and signed at (Dado y firmado en)

St. Louis

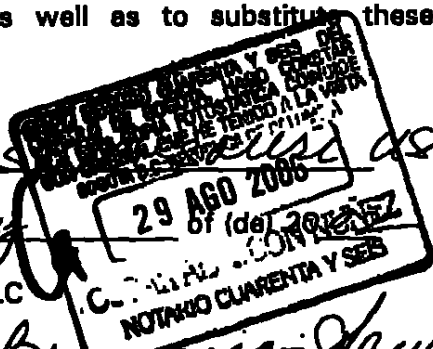
this (a los) 9th day of (dias de)

January

MONSANTO TECHNOLOGY LLC

Por (By)
Título (Title)

Barbara Bunning-Stevens
Barbara Bunning-Stevens,
Intellectual Property Counsel



187

Estados Unidos de América)
 Estado de) SS
 Condado de)

United States of America)
 State of MISSOURI) SS
 County of ST. LOUIS)

Hoy de de 20 , compareció
 , a quien conozco y de

On this ^{9th} day of January of 2002
 personally came

Barbara Bunning-Stevens

quien me consta que firmó el anterior
 documento, y quien debidamente juramentado
 declaró y dijo que él es

to me known, and known to me to be the person
 who signed the foregoing instrument, who being
 by me duly sworn did depose and say that she is
 the Intellectual Property Counsel

de

of Monsanto Technology LLC

la compañía nombrada en el documento, que
 antecede, una sociedad debidamente organizada
 y existente conforme a las leyes del Estado de

the company named within, a limited liability
 company organized and existing under the laws
 of the State of Delaware, United States of
 America, domiciled at the City of Creve Coeur

Estados Unidos de America, domiciliada en la
 ciudad de
 Condado de
 Estado de , Estados
 Unidos de América y legalmente constituida para
 un período de duración que aún no ha
 determinada; que el declarante está autorizado
 por dicha Compañía para conferir este poder; que
 el sello estampado por él al pie de tal poder, en
 nombre y en representación de la expresada
 Compañía, es el sello oficial de ella; y que el
 objeto para el cual se confiere este instrumento
 está comprendido dentro del de la sociedad.

County of St. Louis
 State of Missouri
 United States of America, and legally constituted
 for a period of tenure not yet expired; that the
 deponent is authorized by said Limited Liability
 Company to confer this power of attorney; that
 the seal affixed hereunto by the deponent in the
 name and on behalf of said Limited Liability
 Company is the seal thereof; and that the
 purpose for which this instrument is granted is
 included within the corporate purposes of the
 Limited Liability Company.

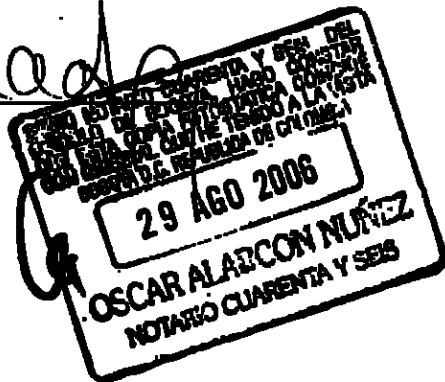
El suscrito notario ha visto los estatutos de
 incorporación firmados en
 Estado de
 con fecha , y certifica que de
 conformidad con la legislación de dicho Estado la
 anterior declaración juramentada es prueba
 suficiente de que los hechos sobre que ella versa
 son ciertos o verdaderos, de lo cual da fe.

The undersigned Notary Public has seen the
 Certificate of Formation of the said Limited
 Liability Company executed at Wilmington
 State of Delaware, under date of March 2, 2000
 and hereby certifies that under the laws of said
 State the foregoing acknowledgment is sufficient
 proof that the facts therein contained are true,
 which she attests.

(Seal)



Caitlin E. Macagy
 Notary Public
 (Notario Público)



Hef
188

**TRADUCCION AL ESPAÑOL del Documento de Poder otorgado por
MONSANTO TECHNOLOGY LLC, domiciliada en 800 North Lindbergh
Boulevard, St. Louis, Missouri, Estados Unidos de América.**

APOSTILLA

(Convención de La Haya del 5 de octubre de 1961)

1. País: Estados Unidos de América

Este documento público

2. ha sido firmado por CAITLIN E. MACAGY

3. actuando en capacidad de NOTARIO PUBLICO

**4. lleva el sello/timbre de CAITLIN E. MACAGY – NOTARIO PUBLICO –
ESTADO DE MISSOURI**

Certificado

5. en Jefferson City, Missouri

6. el 28° día de Enero de 2002

7. por Matt Blunt, Secretario de Estado, Estado de Missouri

8. No. 70695

9. Sello/Timbre

10. Firma

(Firma)

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-039593-00000-0000

Fecha: 2007-04-20 15:58:48 Dep. 2020 NUECREACION
Tra. 11 PATENTEIYII Eje: 379 FASENACIONALI
Act. 411 PRESENTACION Folios: 186

SUPERINTENDENCIA

REQUISITOS MINIMOS PARA ADMISION A TRAMITE
PCT

PATENTE DE INVENCION

[1]

MODELO DE UTILIDAD

[]

- ◆ Indicación de que se solicita la concesión de una patente [1]
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud [1]
- ◆ Descripción de la invención [1]
- ◆ Dibujos de ser estos pertinentes [1]
- ◆ Comprobante de pago de las tasas establecidas [1]

COMPLETA []

INCOMPLETA []

DISEÑO INDUSTRIAL []

- ◆ Indicación de que se solicita el registro de Diseño Industrial []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica y fotográfica del Diseño Industrial o muestra del material que incorpora el diseño []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

ESQUEMA DE TRAZADO []

- ◆ Indicación de que se solicita el registro de un Esquema de Trazado []
- ◆ Datos de identificación del solicitante o de la persona que presenta la solicitud []
- ◆ Representación gráfica del esquema trazado []
- ◆ Comprobante de pago de las tasas establecidas []

COMPLETA []

INCOMPLETA []

Eduar Naranjo

Firma Responsable

Fecha

20-04-07

Carrera 13 No. 27-00 Piso 5, 7 y 10

Conmutador: 3 82 08 40

Fax: 350 52 20

E-mail: info@slc.gov.co

www.slc.gov.co

Bogotá, D.C., Colombia

REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
CADENA BARMIENTO JUAN PABLO
Apoderado(a) y/o Representante de
MONSANTO TECHNOLOGY LLC.

REFERENCIA	Radicación No.	7 39593
	Solicitud internacional	PCT/US2005/034076
	Fecha inicio fase nacional	23/04/2007
	Trámite	11
	Evento	379
	Actuación	438
	Oficio No.	5048

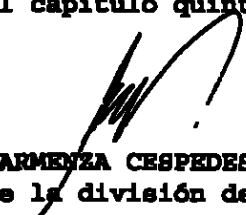
Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

1. La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486.

2. Debe aclarar el nombre del solicitante, por cuanto la publicación internacional difiere del petitorio presentado en fase nacional.

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Unica No.10 de 2001.


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la división de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de fecha 04 MAYO 2007
adpall