



Industria y Comercio

SUPERINTENDENCIA

Delegatura de propiedad Industrial

División de Nuevas Creaciones

PCT

SOLICITUD

PATENTE DE INVENCION

21. EXPEDIENTE No.

05-122665

54. TÍTULO

Sistemas Homogeneos a base de
Sacaroso liquido y aceite

51. CLASIFICACIÓN INTERNACIONAL

71. SOLICITANTE

ICI Americas INC

DOMICILIO

Delaware, Estados Unidos

74. APODERADO

Dilia Rodriguez D'Aleman

22. BOGOTÁ, D. C.,

Dic 2/05

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) LICITANTE (71)	Nombre: ICI AMERICAS INC. Dirección: 1000 Uniquema Boulevard, New Castle, Delaware 19720, Estados Unidos Nacionalidad o domicilio: Delaware, Estados Unidos Lugar de constitución: Delaware, Estados Unidos		IDENTIFICACIÓN C.C. ☐ NIT: ☒ C.E. ☐ OTRO ☐ Cual _____ NÚMERO _____
	Teléfono: _____ Fax: _____ E. Mail: _____		
3) REPRESENTANTE O APODERADO	Nombre: DILIA MARÍA RODRÍGUEZ D'ALEMAN Dirección: Carrera 11 N°. 86-53 Piso 6 Bogotá D.C. Teléfono: 6181088 Fax: 6350824 E. Mail: info@clarkemodet.com.co		IDENTIFICACIÓN C.C. ☒ NIT: ☐ C.E. ☐ OTRO ☐ NÚMERO: 41.654.882 TP: 20824 CSJ
4) INVENTOR (ES) (72)	Nombre: Gregory James LINDNER. Dirección: 18 Hayloft Circle, Wilmington DE 19808. Nacionalidad o Domicilio: Estados Unidos de America.		
5) PCT (86) Solicitud Internacional No. PCTUS/2004/014401 Fecha: Mayo 7, 2004 Publicación Internacional No. WO 2004/100661 A2 Fecha: Noviembre 25, 2004			
6) Título (54) SISTEMAS HOMOGENEOS A BASE DE SACARIDO LIQUIDO Y ACEITE			
7) Clasificación Internacional: <u>A01N25/02; A01N25/02; 43/08; 57/20</u>			
8) PRIORIDAD SI ☒ NO ☐	33) País de Origen Estados Unidos	(32) Fecha Mayo 7, 2003	(31) Número de Solicitud 10/431616
9) Comprobante de pago N°. 05-90.625 Fecha: Noviembre 25, 005			
Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina			

10)

ANEXOS

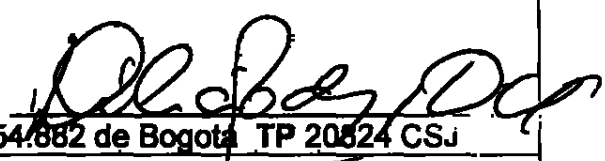
- ☒ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Comprobante de pago por reivindicación de prioridad
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona Jurídica
- ☒ Poderes, si fuera el caso
- ☐ Documento de cesión del inventor al solicitante o a su causante
- ☐ Declaraciones
- ☒ Copia de la solicitud Internacional. (Resumen, descripción, reivindicación, Dibujos).
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicación, Dibujos)
- ☐ Copia 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 12 x 12 y 6 x 6 cm
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionados parcial o totalmente con la invención de esta solicitud.
- ☒ Otros:
1. Reporte búsqueda internacional
 2. Opinión escrita
 3. Solicitud PCT
 4. Transmisión documento prioridad.

11) FIGURA CARACTERÍSTICA:

12) Solicitud concesión de la patente,

NOMBRE: DILIA RODRÍGUEZ D'ALEMAN

FIRMA:


C.C. 41.654.882 de Bogotá TP 20524 CSJ

Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta página

83

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 90,625
FECHA : NOVIEMBRE 25 DE 2005

SUPERINDUSTRIA Y COMERCIO
Radicacion : 05122665 00000000 Folios: 76
Fecha (AMD): 2005-12-02 16:25:46
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE MODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	42212701	25/11/2005	4,397,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
1		TRAMITES DE SOL. DE PATENTE DE IN	443,000.00
		TOTAL :	\$ 443,000.00

SON: CUATROCIENTOS CUARENTA Y TRES MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

7-449 ①

4

TRADUCCIÓN OFICIAL No. 02/305 de un documento escrito en inglés, el cual para su identificación se sella con el sello del traductor al tiempo con la presente. Esta traducción ha sido preparada por Juan Pablo Piedrahita Aguilera, Traductor e Intérprete Oficial debidamente reconocido de conformidad con el Certificado de Idoneidad Profesional No. 0045 expedido por la Universidad Nacional de Colombia.

(Se traduce una Certificación Notarial y Apostilla No. A158741, escritos en inglés, adjuntos a un poder otorgado por ICI AMERICAS INC, escrito en inglés y español con fecha Septiembre 19, 2002)

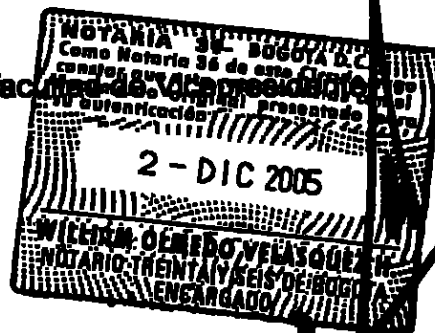
(En español e Inglés Poder)

CERTIFICADO NOTARIAL (Cuando el Solicitante es una Sociedad)

(Poderes otorgados en El Salvador, México, Estados Unidos de América y Venezuela)

Expedido hoy 19 de Septiembre, 2002, el suscrito Notario CERTIFICA que:

- 1) William J. Hutchinson (nombre de la persona que firma el poder), mayor de edad y domiciliado en Princeton, New Jersey, suscribió el anterior documento.
- 2) El otorgante le es conocido personalmente y tiene facultad legal para firmar el documento.
- 3) El otorgante ha suscrito el anterior documento en su facultad de vicepresidente



TRADUCCION OFICIAL No. 02/305
JUAN PABLO PIEDRAHITA AGUILERA
TRADUCTOR E INTERPRETE OFICIAL
C. IDONEIDAD 045
UNIVERSIDAD NACIONAL DE COLOMBIA

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de la persona jurídica ICI Americas, Inc.

4) La mencionada persona jurídica con domicilio comercial en Bridgewater, New Jersey, está debidamente constituida, tiene actualmente existencia legal y el fin para el cual se otorga este poder se encuentra dentro de su objeto social.

5) El otorgante tiene en efecto la idoneidad referida y su representación es legal y está autorizado para otorgar este poder.

6) Fundamento las certificaciones 3), 4) y 5) en los documentos auténticos que para tal fin me fueron exhibidos.

(Firmado) BARBARA A. McHUGH

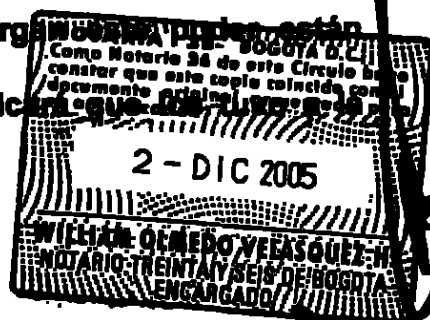
Notario Público

(Sello Notarial a Tinta: BARBARA A. McHUGH Notario Público de New Jersey, Mi Comisión Vence 10/25/04)

(Sello Notarial en Relieve)

Nota: a continuación el Consulado Colombiano debe legalizar la firma del Notario Público

Para todos los demás países el Señor Cónsul de Colombia o ante quien se otorgue, debe expedir una certificación dejando constancia de: 1) la existencia legal de la sociedad, 2) que cumple actualmente con su objeto social, y 3) que la persona o personas que otorgan este poder están facultadas para hacerlo. El Cónsul también certificará que esta copia coincide con el documento original.



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vista los documentos que prueban y acreditan tales circunstancias.

APOSTILLA

(Convenio de la Haya de Octubre 5 de 1961)

1. País: ESTADOS UNIDOS DE AMÉRICA
2. Este documento público ha sido firmado por BARBARA A MCHUGH
3. Actuando en calidad de NOTARIO PÚBLICO DE NEW JERSEY
4. Lleva el sello/estampilla del BARBARA A MCHUGH, NOTARIO

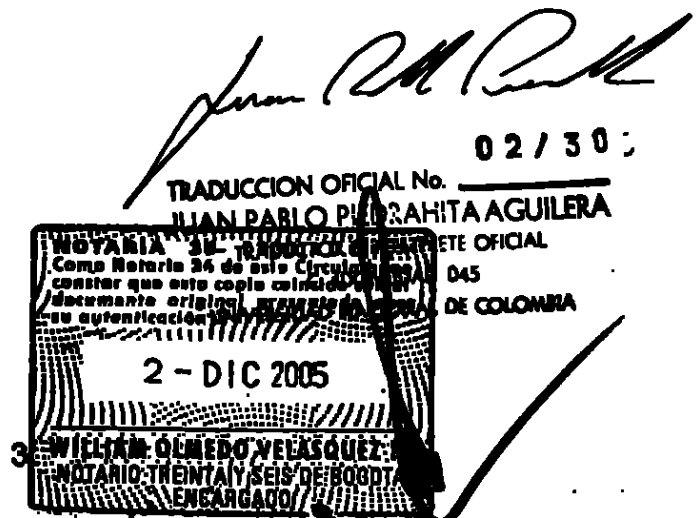
CERTIFICADO

5. En Trenton, New Jersey
6. Hoy 24 de Septiembre, 2002
7. Por el John E. McCormac, CPA, TESORERO de NEW JERSEY
8. No. A158741
9. Sello (Sello de Oblea)

Firma (Firmado)

ES TRADUCCIÓN FIEL Y COMPLETA de la cual se deja copia en los archivos de esta oficina para su confrontación y a la cual me remito.

Bogotá, Octubre 15 de 2002



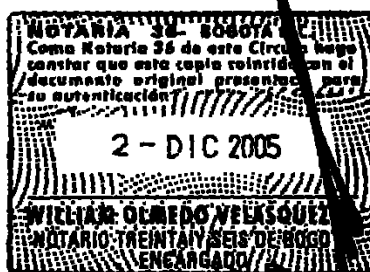
NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2002 OCT 17 A 10:10

PLS
JEFE DE LEGALIZACIONES
SALA DE BOGOTA D.C.

MINISTERIO DE RELACIONES
EXTERIORES

516872
Jon Piedrahita
CUYA FIRMA APARECE EN EL
DOCUMENTO DESEMPAÑA
LAS FUNCIONES INDICADAS



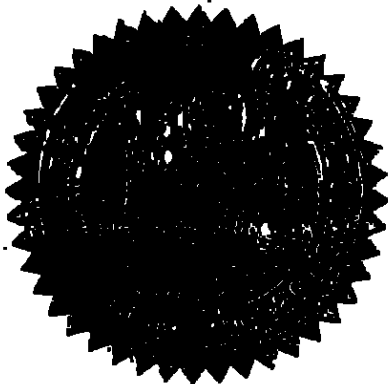
APOSTILLE

(CONVENTION DE LA HAYE DU 5 OCTOBRE 1961)

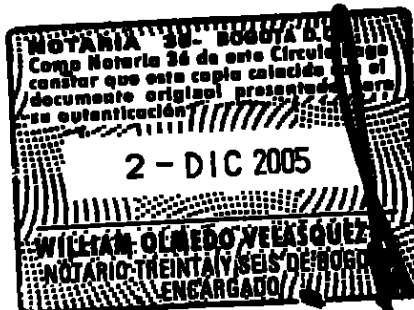
1. COUNTRY: UNITED STATES OF AMERICA
2. THIS PUBLIC DOCUMENT HAS BEEN SIGNED BY:
BARBARA A MCHUGH
3. ACTING IN THE CAPACITY OF:
NOTARY PUBLIC OF NEW JERSEY
4. BEARS THE SEAL/STAMP OF:
BARBARA A MCHUGH, NOTARY

CERTIFIED

5. AT TRENTON, NEW JERSEY
6. THE 24TH DAY OF SEPTEMBER 2002
7. BY: John E McCormac, CPA, NEW JERSEY TREASURER
8. NO. A158741
9. SEAL/STAMP:
10. SIGNATURE



John E McCormac



Clarke, Modet & Co. Colombia Ltda.

PROPIEDAD INDUSTRIAL y DERECHOS DE AUTOR

Apartado Aéreo 92397

Santa Fe de Bogotá, Colombia

PODER

Yo (nuestros), abajo firmante(s)

William J. Hutchinson

en mi (nuestro) carácter de representante(s) legal(es) de

ICI Americas Inc.

una sociedad organizada y existente de acuerdo con las leyes de

New Jersey.

y en actual cumplimiento de su objeto social, con domicilio en

por el presente instrumento confiero (conferimos) poder especial a favor de DILIA MARIA RODRIGUEZ DALEMAN, con Cédula de Ciudadanía No. 41.654.882 de Bogotá y tp. 20824 y CLAUDIA LUCIA CARO RAMIREZ, con Cédula de Ciudadanía No. 40.017.374 de Tunja, y tp. 36448, con domicilio en Santa Fe de Bogotá, Colombia, para que actuando en su orden en nombre del (de la) otorgante le (le), representen ante cualquier entidad, autoridad y/o persona, especialmente ante las del orden Administrativo, Contencioso Administrativo, Judicial, Tribunales de Arbitramento y/o cualquier otro en lo referente a los siguientes asuntos:

1) Solicitar, tramitar, obtener y/o registrar cualquiera de las modalidades de Propiedad Industrial, tales como: patentes de invención, modelos de utilidad, diseños industriales, variedades vegetales, marcas, lemas, nombres y enseñas comerciales y denominaciones de origen; así como sus renovaciones, prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.

2) Solicitar, tramitar, obtener y/o registrar derechos de autor, en cualquiera de sus presentaciones así como la protección de secretos industriales y know-how.

3) Solicitar, tramitar, obtener y/o registrar registros sanitarios, permisos y/o licencias de funcionamiento; así como sus renovaciones o prórrogas, transferencias, cambios de nombre y/o domicilio, contratos y licencias.

4) Ejercer acciones de oposición, observación, reclamos, reconsideración, reposición, apelación, cancelación administrativa o judicial, nulidad, protección al consumidor, concesión de licencias, protección de secretos industriales y demás acciones y recursos relacionados con derechos derivados de los asuntos arriba mencionados y en contra de la competencia desleal, acciones derivadas de la obtención o explotación de licencias, acciones de indemnización de perjuicios. También podrá(n) intervenir en juicios civiles, comerciales, penales, contencioso-administrativos, tutela y de policía; en acciones o juicios promovidos por el (la) mandante o en contra el (ella).

5) Registrar nombres de dominio ante la entidad competente.

6) En el ejercicio de este mandato los mandatarios arriba mencionados quedan facultados para: conciliar, cancelar, transigir, comprometer en árbitros, desistír, recibir y tomar posesión de la cosa objeto de litigio y renunciar o desistír a derechos concedidos o en curso de concesión, admitir los hechos del proceso.

7) Ratificar o no la agencia oficiosa.

8) Así mismo faculto (facultamos) a los mencionados apoderados para recibir notificaciones y designar apoderados judiciales o extrajudiciales, sustituir el presente poder y revocar las sustituciones que hicieren.

Dado y firmado en

a los

días de

de



Firma y signature

William J. Hutchinson, Vice President

POWER OF ATTORNEY

I (we), the undersigned

William J. Hutchinson

legal representative(s) of

ICI Americas Inc.

an organization existing under the laws of

the State of New Jersey

and in present execution of its business activity, domiciled at

10 FINDERNE AVENUE, BRIDGEWATER, NEW JERSEY 08807

do hereby grant POWER OF ATTORNEY to DILIA MARIA RODRIGUEZ DALEMAN, Identification card No. 41.654.882 of Bogotá, and tp. 20824 and CLAUDIA LUCIA CARO RAMIREZ, tp. 36448, Identification card No. 40.017.374 of Tunja, residing in Santa Fe de Bogotá, Colombia, to act in the order of their appointment in behalf of grantor before any entity, authority and/or natural or juridical person, specially before those Administrative, Administrative-Contentious, Judicial, Arbitration courts, and/or any other, in all matters concerning the following:

1) To apply, process, obtain and/or register any of the modalities of Industrial Property, such as: Patents of Invention, Utility Models, Designs, vegetal varieties, Marks, Slogans, Trade Names and emblems and appellations of Origin, as well as their renewal, extensions, assignments, changes of name and/or domicile, agreements and licenses.

2) To apply, process, obtain and/or register copyrights of any kind as well as protection of industrial secrets or know-how.

3) To apply, process, obtain and/or register sanitary registrations, operating authorizations and/or licenses as well as their renewal or extensions, assignments, changes of name and/or domicile, agreements and licenses.

4) To bring actions of opposition, observations, claims, reconsideration, appeal or legal remedies, cancellations, nullity, protection to the consumer, granting of licenses, protection of trade secrets and other actions related with rights derived from the above-mentioned matters and against the unfair competition, actions resulting from the obtaining or exploitation of licenses, recovering damages actions. They can also intervene or participate in Civil, Commercial, Criminal or Contencioso-Administrative litig; the actions for writ mandamus, police actions; in actions, lawsuits, or litigations instituted by the grantor or against him.

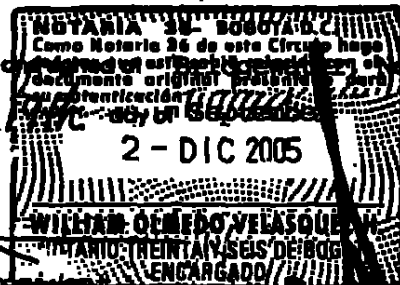
5) To register domain names before the competent entity.

6) To the effect of this mandate the above-named proxy are empowered to: conciliate, cancel, settle, submit to arbitration, withdraw and to receive and take possession of the litigation related object and waive or renounce the rights granted or in process of granting, admit the facts of the case.

7) To ratify or not the officious agency.

8) I (we) hereby appoint the above mentioned attorneys with power to receive notifications and to designate judicial and extrajudicial attorneys, substitute this Power of Attorney and to revoke such substitutions.

Granted and signed in this Public Instrument in New Jersey on this 2nd day of September of 2002



CERTIFICADO NOTARIAL (Cuando el solicitante es SOCIEDAD)

(Poderes otorgados en: El Salvador, Estados Unidos, México y Venezuela)

A los _____ días del mes de _____
de _____, el Notario que suscribe DA FE de
que:

1. _____
(nombre de la persona que firma el poder)

mayor de edad y domiciliado _____
firmó de su puño
y letra el documento que antecede.

2. Conoce al (a la) otorgante y que este (a) está
legalmente capacitado para el otorgamiento.

3. El otorgante ha firmado el referido documento en
su carácter de _____
de la persona jurídica _____

4. La citada persona jurídica con sede en _____
está
legalmente constituida, que tiene actualmente
existencia legal y que el acto para el cual se ha
otorgado este poder está comprendido entre los que
constituyen su objeto social.

5. El otorgante tiene efectivamente la representación
que ostenta, que esta es legítima y que está
facultado para otorgar este poder.

6. las anteriores certificaciones de los puntos 3, 4 y 5, me
constan porque he tenido a la vista los
documentos auténticos.

Notario Público

NOTA: A continuación de lo anterior, el Consul de
Colombia debe autenticar la firma del Notario Público.

CERTIFICADO NOTARIAL (Cuando el solicitante es INDIVIDUO)

A los _____ días del mes de _____
de _____, el Notario que suscribe DA FE de
que:

1. _____
(nombre de la persona que firma el poder)

mayor de edad y domiciliado en _____
firmó en su presencia
el documento que antecede, conoce al otorgante
y que este está legalmente capacitado para el
otorgamiento.

Notario Público

NOTA: A continuación de lo anterior, el Consul de
Colombia debe autenticar la firma del Notario Público.

Para todos los demás países el Señor Consul de
Colombia o ante quien se otorgue, debe expedir una
certificación dejando constancia 1) de la existencia
legal de la sociedad, 2) de que esta ejerce actualmente
su objeto social, y 3) de que la persona o personas que
otorgan el poder están facultadas para hacerlo, dejando
constancia así mismo de que tuvo a la vista las pruebas
que acreditan tales circunstancias.

TRADUCCION OFICIAL No. _____
JUAN PABLO PIEDRAHITA AGUILERA
TRADUCCION E INTERPRETE OFICIAL
C. ID. 11.173.045
UNIVERSIDAD NACIONAL DE COLOMBIA

NOTARIAL CERTIFICATE (When the applicant is a CORPORATION)

(Powers of attorney granted in: El Salvador, Mexico, U.S.A. and Venezuela)

This 19th day of September, 2002
the undersigned Notary CERTIFIES that

1. William J. Hutchinson
(name of the person who signs the power of attorney)

of legal age and domiciled
in Princeton, New Jersey set
his hand on the foregoing document.

2. The grantor is to him personally known and that
he/she has legal capacity to execute the document.

3. The grantor has executed the foregoing document
in his capacity of Vice President
of the juridical person
ICI Americas Inc.

4. The mentioned juridical person with place of
business in Bridge Water, New Jersey
is duly organized, has actual legal existence and that
the purposes for which the power of attorney is granted
are within the scope of its corporate purposes.

5. The grantor has in fact the referred quality and
that his/her representation is legal and that he/she
is empowered to grant this power of attorney.

6. I have based the above certifications 3, 4 and 5, on
the authentic documents which William J. Hutchinson
were exhibited to me.

Barbara M. Hughes
Notary Public

NOTA: Then the Colombian Consul must legalize the
signature of the Notary Public.

NOTARIAL CERTIFICATE (When the applicant is an INDIVIDUALS)

On this _____ day of _____
the undersigned Notary CERTIFIES that:

1. _____
(name of the person who signs the Power of Attorney)

of legal age and domiciled at _____
signed in his presence
the foregoing document. the grantor is to him
personally known and that he/she has legal capacity to
execute the document.

Notary Public

NOTA: Then the Colombian Consul must legalize the
signature of the Notary Public.

For all other countries the Colombian Consul or before
who it is granted must issue a certification stating 1) the
legal existence of the corporation, 2) that the corporate
purposes are actually being accomplished, 3) that the
person or persons who grant the Power of Attorney are
empowered to do so, and 4) that the documents
presented to me were authentic. I have based the above
certifications on the documents which William J. Hutchinson
were exhibited to me.

02/3

2 - DIC 2005

WILLIAM OLMEDO VELASCO
NOTARIO TREINTAYSEIS DE AÑOS
ENGAÑADO

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 November 2004 (25.11.2004)

PCT

(10) International Publication Number
WO 2004/100661 A2

(51) International Patent Classification: A01N 25/02

(21) International Application Number:
PCT/US2004/014401

(22) International Filing Date: 7 May 2004 (07.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10431,616 7 May 2003 (07.05.2003) US

(71) Applicant (for all designated States except US): ICI
AMERICAS, INC. [US/US]; 10 Pinderne Avenue,
Bridgewater, NJ 08807 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): LINDNER, Greg, J.
[US/US]; 18 Hayloft Circle, Wilmington, DE 19808 (US).

(74) Agent: SHARER, Paul, L.; Intellectual Property Group,
Mayer Brown Rowe & Maw LLP, 1909 K Street, N.W.,
Washington, DC 20006-1101 (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, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, 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, 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, IE, IT, 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).

Published:

— without international search report and to be republished
upon receipt of that report

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

(54) Title: HOMOGENEOUS LIQUID SACCHARIDE AND OIL SYSTEMS

(57) Abstract: Oil based emulsifiable concentrates containing a liquid saccharide including a) at least one oil component; b) at least one saccharide, particularly a liquid saccharide solution (LS); c) and at least one non-ionic surfactant. The concentrate may also contain at least one of d) at least one surfactant hydrocarbyl saccharide; or e) at least one anionic surfactant; or f) at least one additional oil soluble non-ionic surfactant. The concentrates are typically homogeneous for at least 24 hours and emulsify readily on dilution into water. The concentrates may also contain an antifoaming agent especially a polysiloxane. Upon dilution in water, the emulsions formed from the concentrates are applied to substrates in combination with agrochemically active ingredients, preferably N-phosphonomethylglycine in the form of its soluble salts, to control weeds.

WO 2004/100661 A2

HOMOGENEOUS LIQUID SACCHARIDE AND OIL SYSTEMS

Background of the Invention

[0001] Agrochemical compositions have been used to improve the quality and quantity of farm grown products. In this regard they can enhance biological activity and act as nutrients, growth regulators and/or pesticides, for instance as herbicides, insecticides, fungicides, or acaricides. However, since they are expensive to make and purchase, it is desirable to reduce their overall cost in use by improving their effectiveness in a unit area treated with the agrochemical.

[0002] In order to improve or enhance the effectiveness of many agrochemicals, certain materials are added to water-based agricultural spray mixtures containing the agrochemical and concurrently applied to agricultural substrates. These materials are commonly identified as agricultural spray adjuvants and exist in a wide variety of forms and compositions that are used today in commercial agriculture. These adjuvant products are used to provide a broad array of effects in typical use including, but not limited to, foam control, enhancement of the effectiveness of a specific agrochemical, and/or modification of the agricultural spray mixture for either improved stability or modulation of spray droplet diameter.

[0003] In the United States, most economically advantageous adjuvant products used to improve or enhance the efficacy of an agrochemical, primarily a pesticide, are supplied as liquids. The preferred liquid adjuvant products (for both convenience and economy) manufactured and sold in the US are supplied as concentrated liquids and fall into two primary categories. These categories are: (1) self-emulsifying oil and surfactant compositions more commonly identified as Crop Oil Concentrates (COC), and (2) readily water soluble or dispersible surfactant formulations known as concentrated liquid Non-Ionic Surfactants (NIS). Commercial distribution channels in the US efficiently transport large volumes of such products, primarily in bulk form, making COC and NIS type products very economical for their intended use. By improving the efficacy of the more costly pesticide through its combination in spray mixtures with an economically advantageous, primarily low cost, adjuvant product, the overall economics of commercial agriculture can be improved. Use of effective adjuvant products in this manner decreases the seasonal cost to produce

agricultural commodities and may also improve commodity yields, offering economic benefits to those who use them.

[0004] One of the largest single groups of such effective liquid adjuvant products sold in the United States (by volume) is a COC composition containing between 60 and 90% of a suitable agricultural grade of mineral oil; an alternate form of this adjuvant type contains a vegetable oil or methylated seed oil. All commercially significant forms of this adjuvant type commonly contain an oil soluble emulsifier composition composed of a blend of anionic and/or non-ionic surfactants that provides self-emulsification of the oil component upon dilution in a water-based agricultural spray mixture; the total surfactant concentration in a typical COC product can range from 1 to 40%, most typically between 10 and 17%.

[0005] While the oil and surfactant composition in a COC adjuvant product could also be offered as a pre-emulsified system in water (an oil-in-water emulsion), the added cost of production for an emulsified adjuvant product tends to make it less economically advantageous than the equivalent volume of oil adjuvant offered as a COC. Water based systems also have the undesirable characteristics of being generally more complicated to develop and manufacture and of requiring the use of discrete thickening, preserving, and anti-freeze systems due to the tendency of water based emulsions to support microbial growth, cream or settle/sediment, and deteriorate over time or during the freeze-thaw cycle. The effect of including water as the dispersing medium also dilutes the active components (oil and surfactant composition) making the system more expensive to deliver in the field on a pound of "active" adjuvant basis. Logistics costs also increase on this basis as more water is shipped than may otherwise be present in a comparable COC type system.

[0006] In recent times, there have been specific improvements upon the cost-effectiveness of the described economically advantageous crop oil concentrates. Most of these improvements have focused on two aspects of the composition. The first aspect is increasing the total concentration of oil soluble surfactant emulsifier which has resulted in a change in preferred surfactant concentration from 12-17% ten years ago to approximately 40% at the current time; this change was associated with a reduction in the amount of COC adjuvant product applied per unit area and resulted in improved cost-in-use attributes for the adjuvant. The second aspect is the selection of specific surfactant types based on both field data and scientific judgement; this change was associated with improved performance of the adjuvant

product with specific pesticide products. PCT Publication WO 95 03881 by Auda et al describes an agrochemical crop oil concentrate containing an oil or oils, hydrocarbyl saccharide surfactant, and additional non-ionic surfactant that emulsifies readily upon dilution in water. This COC adjuvant composition was associated with enhancement or improvement of weed control performance in conjunction with with soluble salts of N-phosphonomethylglycine.

[0007] More recently, US 5,945,377 to Penner describes compositions incorporating a postemergence herbicide and a monosaccharide, particularly fructose, as a potentiator of the herbicide against weeds without decreasing tolerance of a crop plant to the herbicide. The compositions are used as a spray in water in a method for killing weeds. Although not considered an NIS adjuvant, corn syrup was evaluated as an adjuvant with several postemergence herbicides in the greenhouse and field studies. The greatest enhancement of herbicide activity was observed with high fructose corn syrup applied in combination with an ammonium sulfate and an effective non-ionic adjuvant with anionic herbicides such as glyphosate and glufosinate for control of grass species such as giant foxtail. The efficacy of the corn syrup as an adjuvant was both weed and herbicide specific.

[0008] The previously mentioned publication (WO 95 03881) describes self-dispersing alkylpolysaccharide surfactants in crop oil concentrates (COC's). These compositions did not include additional aqueous liquid non-surfactant polysaccharide components which have been found recently to promote the herbicidal activity of glyphosate. It was concluded that a robust, single phase composition containing: (1) an oil adjuvant, (2) a saccharide adjuvant, and (3) an optimal amount of surfactant with a corresponding minimum of additional water could allow the delivery of a highly concentrated liquid agricultural adjuvant product with a total surfactant concentration similar to those in use today (ca. 10 - 40% w/w). The successful incorporation of the inexpensive and efficacious saccharide adjuvant would improve the cost-effectiveness of the finished adjuvant product. The resulting product is commercially advantageous for the manufacturer and economically beneficial to the purchaser/user. An additional advantage for combining the saccharide and surfactant adjuvant composition with the traditional COC adjuvant composition would be the significant commercial advantage obtained by being able to provide one very broadly effective adjuvant composition having the preferred characteristics of the COC, NIS, and newer saccharide adjuvant types.

[0009] The compositions described are intended as commercial alternatives to traditional 17 and 40% surfactant in oil based COC adjuvants used in the agricultural market. These COC adjuvant types, although cost-effective for use with most water-dispersible agrochemicals, are not the most effective type of adjuvant for the soluble salts of N-phosphonomethylglycine, most commonly called glyphosate, which represents the largest commercial pesticide sold in the US and as a result presents the largest single adjuvant sales opportunity. The most efficacious NIS adjuvants for use with glyphosate, identified as ethoxylated tallow alkylamines, are for the current time typically combined into concentrated glyphosate solution products and are therefore not readily accessible to adjuvant products intended for combination into agricultural spray mixtures. With the expiration of patents on concentrated glyphosate salt solution products, other forms of the pesticide, including products which intentionally do not include the preferred NIS adjuvant as a means to reduce the cost of formulated glyphosate and increase its concentration in solution products may also become available. It would be advantageous to alter the traditional COC product or the COC product described in WO 95 03881 to demonstrate improved efficacy enhancement with glyphosate products; this would be highly desirable as a means of expanding the market for the highly cost-effective COC adjuvant product.

[0010] Ideally it is desirable to achieve a surfactant composition that serves as both the combined COC adjuvant self-emulsifier and compatibilizer/stabilizer for the saccharide component and which also has the ability to stabilize and self-emulsify the oil alone (without the saccharide component) as well as having special advantages in that it offers improved economies in the purchase of a single surfactant composition and in enabling the flexible manufacturing of COC adjuvants in the same surfactant composition both with and without added liquid saccharide components. Since the corn syrup adjuvant also requires concurrent application of a nonionic surfactant adjuvant for optimum performance, the direct combination of the oil and corn syrup with a single surfactant system that would both "activate" the saccharide and concurrently emulsify the oil component would have the greatest economic and competitive advantage. Essentially, by using the combined COC and saccharide NIS product concept, the composition would be 100% active with a minimum total concentration of the surfactant composition required for optimum performance. Since the surfactant constitutes the most costly input for manufacturing on a component purchased

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price (per pound) basis, reducing surfactant to the minimum required for optimal activity is highly desirable.

[0011] The greatest difficulty in developing the combined saccharide COC adjuvant product is the identification of suitable surfactant systems which would enable the formulation of homogeneous compositions that would function both as robust stabilizers for a highly concentrated liquid saccharide solution in an oil adjuvant and which would provide the self-emulsification upon dilution that is required. These two opposing effects must be delivered in one adjuvant product with a minimum of total surfactant. Preferably a foam control agent would also be included in the composition.

[0012] In US 5,885,646 to Wong, there is described a process for preparing nut spreads having a sugar level of from about 15 to about 50% and especially flavored nut spreads having such relatively high levels of sugar. A substantially homogeneous blend is prepared from a fluid suspension consisting essentially of an intimate mixture of sugar, liquid oil and lecithin as a surfactant to improve the fluidity of the suspension, a nut solids-containing mixture and a flavorant that is preferably added to the fluid suspension. The resulting flavored nut spreads are more fluid and softer than products made without using the fluid suspension. This invention does not provide for the characteristics of either liquid product homogeneity or self-emulsification and demonstrates a relatively high viscosity, which makes it irrelevant to this invention.

[0013] In US 3,959,498 to Lyall there is described a one step process for applying sugar and an edible fat or oil to cereal bases. No separate step of spraying the oil into the cereal substrate is necessary. The invention also provides an emulsion cereal coating for achieving the above purpose, and a method of preparing said coating. A quantity of edible fats or oils or other edible oil-or fat-derived oleaginous material (5-32%) along with a quantity of emulsifier (0.5-5%) is added to an aqueous sugar solution (60-85% solids) to make up a syrup emulsion having a water content in the range of 9% - 34% by weight. The edible fat or oil and emulsifier are added to the aqueous syrup at a temperature ranging from 115°F, to 155°F (46.1 C to 68.3 C, and after emulsification, the mixture is heated to about 180°F (82.2 C). As in the above example, this invention does not provide for the characteristics of either liquid product homogeneity or self-emulsification and demonstrates a relatively high viscosity, which makes it inapplicable to this invention. In addition it provides for an oil-in-

water emulsion whereas the composition claimed herein is a liquid homogeneous (solution or microemulsion) product.

Summary of the Invention

[0014] The current invention involves the development of cold (0° C), room temperature (about 20 -25° C), and heat (e.g. about 50° C) stable systems comprising mixtures of a concentrated liquid) saccharide product with an agricultural spray oil. These mixtures remain homogeneous liquids within the temperature range of about 0° - 50° C and are self-dispersing upon dilution in oil. The described homogeneous liquids contain amounts of 0.5-50% by weight surfactant with oil:saccharide product ratios between 1:100 and 100:1 with the preferred composition occurring between 1:10 and 10:1; the more preferred composition between 1:3 and 3:1; and the most preferred composition occurring between 1:2 and 2:1.

[0015] The invention comprises the basic components of: a biologically efficacious oil, a liquid saccharide product (which are primarily concentrated, viscous water based syrups), and one or more surfactants to deliver a stable, water dispersible, and homogeneous (solution or microemulsion) delivery system for agricultural adjuvants. One specific surfactant composition or surfactant chemical type is not universally required; using the understanding of interactions that was developed, a broad range of surfactant compositions were developed that were capable of delivering the described product.

[0016] Surfactant compositions that were used to develop such formulations include but are not limited to alkylpolysaccharides, phosphate esters, sorbitan esters, mono- and diglycerides, polysorbates, and ethoxylated alkylamines. Minor amounts of water may be used to effect the compatibilization of oil:surfactant:saccharide systems; in no case was more than 25% water added to effect compatibilization. Surfactant systems providing the desired homogeneity and compatibility were typically used in the range of 10-40% with the more preferred compositions containing 10-35%; and the most preferred compositions containing 10-25%.

[0017] Preferably the surfactant includes a non-ionic surfactant and is most preferably made entirely of one or more non-ionic surfactants. If desired, other surfactants, such as at least one anionic surfactant, for instance an anionic alkanolamine salt may be employed.

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[0018] This invention relates to surfactant compositions and in particular to compositions which contains a plurality of surfactants and at least one oil, and which is readily emulsifiable into water.

[0019] The invention provides a concentrate composition which comprises:

- a) at least one oil component;
- b) at least one non-surfactant saccharide,
- c) at least one non-ionic surfactant.

[0020] The composition may also comprise at least one of the following:

- d) at least one surfactant hydrocarbyl saccharide; or
- e) at least one anionic surfactant; or
- f) at least one additional oil soluble non-ionic surfactant.

Detailed Description of the Invention

[0021] The composition of the invention typically takes the form of an oil-based concentrate which is homogenous for at least 24 hours and which emulsifies readily on dilution into water. It will be used as a precursor for dilution with water for agricultural spray mixtures containing an agrochemical. Such spray mixtures will contain one or more pesticidally active ingredients and/or nutrients.

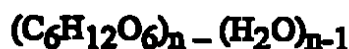
[0022] The concentrate composition may also comprise a water miscible liquid, which may be desirable if the viscosity of the composition would otherwise be inconveniently high. Such liquid may include or be water. The water content is preferably low enough for the composition to remain homogenous for at least 24 hours after being made. The components and their proportions are preferably chosen such that where any components are readily available only as aqueous solutions, such as HFCS (high fructose corn syrup), the composition provided by mixing the composition components is stable, notwithstanding the water which is thereby introduced. When the concentrate composition includes water, the concentrate will usually be a solution of the water in the oil, the surfactant combination acting to solubilise the water, or as a water-in-oil colloidal emulsion or a microemulsion in which the water is dispersed as very fine droplets such that the composition is clear or transparent.

[0023] The oil component typically has a boiling point of over about 200°C at atmospheric pressure and a melting point not higher than about 60°C. It may comprise for example a mineral oil, an optionally hydrogenated vegetable oil, such as an optionally hydrogenated cotton seed oil, linseed oil, mustard oil, neem oil, niger seed oil, oiticica oil, olive oil, palm oil, palm kernel oil, peanut oil, perilla oil, poppy seed oil, rape seed oil, safflower oil, sesame oil, or soybean oil as well as an ester (especially a C₁ to C₆ ester) of a C₈ to C₂₂ fatty acid (especially a C₁₂ to C₁₈ fatty acid) e.g. methyl, ethyl or propyl laurate, myristate, palmitate, palmitoleate, linoleate, linolenolate, stearate or oleate, or a mixture thereof, e.g. an ester in which the total number of carbon atoms in the molecule does not exceed 20, and preferably an ester of a C₁₂ to C₁₈ fatty acid, e.g. methyl, ethyl or propyl laurate, or a mixture thereof.

[0024] The oil component preferably also contains or is associated with at least one oil soluble surfactant, especially one that can render the oil self-emulsifiable into water. Such a surfactant may include at least one of relatively high HLB (hydrophilic lipophilic balance) in combination with one of low HLB, for example calcium stearate. Such an oil solution component may be in the form of a commercially available so-called "crop oil" or "oil adjuvant". A typical oil component contains about 99 to about 45, preferably about 90 to about 60, parts by weight of oil, and about 1 to about 55, preferably about 10 to about 40, parts by weight of oil soluble surfactant(s). When water is present in solubilised form or as a colloidal emulsion or a microemulsion the oil soluble surfactant may be partitioned between oil phase and aqueous phases (or be present at the interface).

[0025] The liquid saccharide solution may be of a monosaccharide, oligosaccharide or a polysaccharide or mixture thereof; saccharides may be linear, branched, or cyclic in nature. For such liquid saccharide solutions, the solvent may be water, propylene glycol, or glycerol or any combination thereof. It is conventional to refer to liquid saccharide solutions as syrups. Oligosaccharides present in solution are commonly identified as maltodextrins while polysaccharides are commonly identified as dextrans. Among liquid saccharide solutions, compounds of particular use in this invention include compounds and mixtures of compounds described as HFCS, corn syrup, corn sweetener, invert sugar, invert sugar syrup, sugar, sugar syrup, and maltodextrins where the resulting liquid saccharide solution is homogeneous and stable for at least 24 hours and contains about 75 parts by weight of water or less, preferably about 15 to about 50 parts by weight of water.

[0026] It is desirable that when the saccharide is an oligosaccharide of the general formula:



where n is greater than or equal to one and not more than fifty. In particular, the saccharide may be one in which the average value of n is typically at least 1 and not more than 5. A particularly useful material of this type is one in which n has an average value of approximately 1 and where the saccharide is a monosaccharide and the monosaccharide is a keto-sugar, most preferably fructose. Fructose is commercially available as HFCS and the material designated for example as IsoClear 55 by Cargill can be used satisfactorily.

[0027] The non-ionic surfactant(s) may be any which will give a composition which is stable and homogeneous for at least 24 hours after being made.

[0028] Preferred non-ionic surfactants are of the formula:



wherein

- R^1 is a hydrocarbyl, hydrocarbonyl, or hydrocarbamidyl group, which suitably contains from 6 to 24, preferably 8 to 22, and especially 12 to 18 carbon atoms, a glycerol or polyglycerol group, or a sorbitan or sorbitol group;
- A is a polyalkylene oxide unit containing an average of n alkylene oxide groups or mixed alkylene oxide groups, where the alkylene groups each have 2 to 8, preferably 2 or 3, carbon atoms;
- n is between 0 and 40, preferably between 2 and 30, and most preferably between 5 and 20;
- R^2 is hydrogen or hydrocarbonyl residue having 8 to 22 carbon atoms, or a polycarboxylic acid residue having 2 to 6 carbon atoms such as malate, fumarate, maleate, succinate, or citrate, or an oligomer thereof;
- R^3 is a hydrocarbyl or hydrocarbonyl group having 8 to 22 carbon atoms, preferably 12 to 18.

[0029] The surfactant hydrocarbyl saccharide may be any which will give a composition which is stable and homogeneous for at least 24 hours after being made.

[0030] The surfactant hydrocarbyl saccharide may be a monoglycoside or a polyglycoside or mixture thereof. It is conventional to refer to hydrocarbyl saccharide surfactants as hydrocarbyl polysaccharides even where the saccharide moiety only contains one saccharide unit. Typically such surfactants are mixtures of compounds with monosaccharide and polysaccharide (including disaccharide) units. Among glycosides, compounds of particular use in this invention include compounds and mixtures of compounds of the formula:



where

R is a hydrophobic moiety;

G is a saccharide residue; and

a has an average value of at least 1.

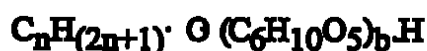
[0031] The group R may be an optionally substituted hydrocarbyl group. In particular R can be an alkyl, cycloalkyl, aryl, alkaryl, aralkyl or alkenyl group and is preferably an alkyl group. The group R suitably contains from 4 to 30 carbon atoms, preferably up to 24 carbon atoms, more preferably from 6 to 18 carbon atoms and especially from 8 to 14 carbon atoms. Thus, R can be a mixture of alkyl or alkoxy groups which contain, on average, for example 8 to 14 carbon atoms.

[0032] The saccharide residue G may be derived from one or more of fructose, glucose, mannose, galactose, telose, gulose, allose, altrose, idose, arabinose, xylose, lyxose and ribose or from mixtures thereof. The group G is conveniently derived from glucose units and the glycoside is then a glucoside. If derived from sucrose the groups will comprise fructose and glucose residues.

[0033] The value of a is the degree of polymerisation. It typically has an average value of at least 1.1, preferably at least 1.2 and especially at least 1.3. The value of a is typically not greater than 8, and preferably not greater than 4, for example not greater than 2. When the glycoside is an alkyl glucoside, the value of a is conveniently between 1 and 2.

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[0034] Desirable results are obtained when the glycoside is an alkyl polyglucoside of the general formula:



where

n is from 8 to 14, and

b is greater than one and not more than two.

[0035] In particular, the glucoside may be one in which the average value of n is from 9 to 13 and especially about 10. The value of b is typically at least 1.3 and not more than 1.9. A particularly useful material of this type is one in which n is from 8 to 11 and has an average value of 10 and b is about 1.35. Surfactant hydrocarbyl saccharides are commercially available and the materials designated for example as Atplus 452 and Atplus 438 by Uniqema or as sold under the trade name Triton BG 10 by Dow Chemicals can be used satisfactorily.

[0036] The anionic surfactant(s) may be any which will give a composition which is stable and homogeneous for at least 24 hours after making up.

[0037] The anionic surfactant(s) may be any which will give a composition which is stable and homogeneous for at least 24 hours after making up. It is characterized as at least one anionic surfactant compound of the general formula:



where

R¹ is a hydrocarbyl group having 6 to 24 carbon atoms, preferably 8 to 22 carbon atoms, and most preferably 12 to 18 carbon atoms;

A is a polyalkylene oxide unit containing an average of n alkylene oxide groups or mixed alkylene oxide groups, where the alkylene groups each have 2 to 8, preferably 2 or 3, carbon atoms;

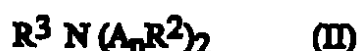
n is between 0 and 60, preferably between 2 and 30, and most preferably between 3 and 15;

X is a group including at least one acidic H atom or salt thereof, desirably an amine salt.

[0038] In the foregoing formula X is a group including at least one acidic atom or a salt thereof, by which is meant that the group X can be ionized to form an anionic group in an aqueous medium. The group thus provides an anionic function, thereby making the surfactant anionic. This function can be a partially or fully oxidized phosphorus, sulfur, or carbon acid group.

[0039] The other non-ionic surfactant(s) may be any which will give a composition which is stable and homogeneous for at least 24 hours after being made.

[0040] Desirable results are particularly obtained when the non-ionic surfactant is of the general formula (I) or (II):



wherein

R^1 is a hydrocarbyl, hydrocarbonyl, or hydrocarbamidyl group, which suitably contains from 6 to 24, preferably 8 to 22, and especially 12 to 18 carbon atoms, a glycerol or polyglycerol group, or a sorbitan or sorbitol group;

A is a polyalkylene oxide unit containing an average of n alkylene oxide groups or mixed alkylene oxide groups, where the alkylene groups each have 2 to 8, preferably 2 or 3, carbon atoms;

n is between 0 and 40, preferably between 2 and 30, and most preferably between 5 and 20;

R^2 is hydrogen or a hydrocarbonyl group having 8 to 22 carbon atoms, or a polycarboxylic acid residue having 2 to 6 carbon atoms such as malate, fumarate, maleate, succinate, or citrate, or an oligomer thereof;

R^3 is a hydrocarbyl or hydrocarbonyl group having 8 to 22 carbon atoms, preferably 12 to 18.

[0041] The relative proportions of the oil component (a), the liquid saccharide solution (b), and the non-ionic surfactant (c) are suitably (by weight):

a) 10 to 90, especially 25 to 75, preferably 30 to 60,

b) 10 to 90, especially 15 to 45, preferably 20 to 40, and

- c) 5 to 80, especially 5 to 60, preferably 10 to 45; and optionally at least one surfactant hydrocarbyl saccharide (d); or anionic surfactant (e); or non-ionic surfactant (f), the proportions are as follows:
- d) 1 to 20, especially 2 to 15, preferably 3 to 10, or
- e) 1 to 20, especially 2 to 15, preferably 3 to 10, or
- f) 1 to 20, especially 2 to 15, preferably 3 to 10.

[0042] Any chemical agent specific to the intended use of the composition will be an agrochemical. The agrochemical is typically one or more nutrients, growth regulators, herbicides, and/or pesticides, for example insecticides, fungicides or acaricides.

[0043] The invention includes a process for making the composition of the invention which comprises mixing the components together.

[0044] The invention further includes a diluted formulation which comprises a composition comprising components (a), (b) and (c) according to the invention with from about 10 to about 10,000 times the weight of the composition of water. The concentrate compositions of the invention emulsify readily on dilution in water to form the formulation. At relatively low levels of dilution, the product will be an oil-in-water emulsion having a relatively high concentration of oil. This intermediate emulsion subsequently can be further diluted by water or an aqueous solution or suspension of other components desired in the final formulation.

[0045] The diluted formulations can be made up in various ways. Thus, a formulation comprising components other than (a), (b), (c) and optionally one or more of components (d), (e), or (f) and water, can be made up by simply mixing the composition of components (a), (b), (c) and optionally one or more of components (d), (e), or (f) with water.

[0046] In a further aspect, the invention provides a method of applying a formulation of the invention to a substrate. Embodiments of this method include a method of treating vegetation by applying to plants and/or soil such a formulation according to the invention which formulation comprises a specific chemical agent which is an agrochemical.

[0047] In this embodiment the agrochemical may be one or more growth regulators, herbicides, and/or pesticides, for example insecticides, fungicides or acaricides. This embodiment of the invention of the method of applying the formulation accordingly includes: a method of killing or inhibiting vegetation by applying the formulation which comprises a specific chemical agent which is one or more growth regulators and/or herbicides, and a method of killing or inhibiting plant pests by applying the formulation which comprises a specific chemical agent which is one or more pesticides, for example insecticides, fungicides or acaricides.

[0048] In this embodiment, the effect of the agrochemical, whether one or more growth regulators, herbicides, and/or pesticides, for example insecticides, fungicides or acaricides, may be potentiated by the oil component and/or the saccharide and/or the surfactant composition present in the composition.

[0049] Examples of the agrochemical which is typically one or more growth regulators, herbicides, and/or pesticides, for example insecticides, fungicides or acaricides, particularly growth regulators, herbicides, etc. include phosphonomethyl-n-carboxymethyl (PMCM) compounds and related compounds of the formula:



where

each R^7 is independently halogen, $-NHOH$, $-N(R^8)_2$, $-OR^9$, $-SR^9$ or $-OM$, where

R^8 is independently a hydrogen, or alkyl or hydroxyalkyl, preferably containing less than about 5 carbon atoms, alkenyl, preferably containing less than about 5 carbon atoms, or phenyl; each R^9 is independently hydrogen, alkyl, hydroxyalkyl or chloroalkyl, preferably containing less than about 5 carbon atoms, alkoxy, preferably containing less than about 5 carbon atoms, alkylene amine, preferably containing less than about 12 carbon atoms, phenyl or benzyl; M is hydrogen or an agriculturally acceptable salt forming moieties such as alkali metal, alkaline earth metal, stannic, ammonium, organic ammonium, alkyl sulfonium, alkyl sulfoxonium, alkyl phosphonium moieties or combinations thereof; and Z is hydrogen, an organic moiety or an inorganic moiety.

[0050] Representative patents disclosing at least some of such compounds include US Patents 3799758, 4397676, 4140513, 4315765, 3868407, 4405531, 4481026, 4414158,

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4120689, 4472189, 4341549 and 3948975. Patents disclosing PMCM compounds wherein Z is other than hydrogen include US Patents 3888915, 3933946, 4062699, 4119430, 4322239 and 4084954.

[0051] In preferred PMCM compounds,
Z is hydrogen or an organic substituent;
R⁹ is independently selected from hydrogen, alkyl, hydroxyalkyl or chloroalkyl, preferably containing less than about 5 carbon atoms, alkoxy, preferably containing less than about 5 carbon atoms, alkylene amine, preferably containing less than about 12 carbon atoms, phenyl or benzyl moieties; and
M is selected from hydrogen and agriculturally acceptable salt forming moieties, alkali metal, phosphonium moieties or combinations thereof.

[0052] Representative patents disclosing at least some of such compounds include US Patents 3799758, 4397676, 4140513, 4315765, 3868407, 4405531, 4481026, 4414158, 4120689, 4472189, 4341549 and 3948975. Patents disclosing PMCM compounds wherein Z is other than hydrogen include US Patents 3888915, 3933946, 4062699, 4119430, 4322239 and 4084954.

[0053] In preferred PMCM compounds, Z is hydrogen or an organic substituent such as methylene carboxylic; methylene phosphonic; and methylene cyano. Other organic substituents include carboxyl, such as formyl, acetyl, benzoyl, perfluoroacyl and thiocarbonyl; ethylene, such as cyano, carbamoyl or carboxy substituted ethyl; and benzene sulphonyl substituents. Patents disclosing compounds where the nitrogen has three organic substituents include US Patents 3455675, 3556762, 3853530, 3970695, 3988142, 3991095, 3996040, 4047927, 4180394, 4203756, 4261727 and 4312662. A preferred tertiary nitrogen substituted PMCM compound is N,N-bis(phosphonomethyl)glycine.

[0055] Those PMCM compounds where Z is hydrogen are most preferred when the phytoactivity desired is herbicidal activity.

[0056] The above listed patents are incorporated herein by reference.

[0057] Illustrative examples of agriculturally acceptable salt forming moieties represented by M, as in OM, are the alkali metals having atomic weights of from 22 to 133, inclusive, such as sodium, potassium, or rubidium; the alkaline earth metals having atomic weights of from 24 through 88 inclusive, such as magnesium or calcium; ammonium and aliphatic ammonium, wherein the aliphatic is primary, secondary, tertiary or quaternary and preferably wherein the total number of carbon atoms does not exceed more than about twelve; phenylammonium; trialkylsulphonium, preferably wherein the total number of carbons in the three alkyl substituents does not exceed more than about six, such as trimethylsulphonium, ethyl dimethylsulphonium, propyl dimethylsulphonium and the like; trialkylsulphoxonium, preferably wherein the total number of carbon atoms in the three alkyl substituent does not exceed more than about six, such as trimethylsulphoxonium, ethyl dimethylsulphoxonium, propyl dimethylsulfoxonium and the like; tetraalkylphosphonium, such as tetramethylphosphonium, ethyl trimethylphosphonium, propyltrimethylphosphonium and similar groups.

[0058] In desirable compositions according to this invention, M is independently selected from the above described agriculturally acceptable salt forming moieties and hydrogen. In more desirable compositions, M is an alkali metal, ammonium, monoalkyl ammonium or trialkylsulphonium moiety. In especially desirable compositions only one M is an alkali metal, ammonium, monoalkyl ammonium, or trialkylsulphonium moiety, while the two M's are hydrogen.

[0059] Particularly desirable compositions include isopropylamine N-phosphonomethylglycine, trimethylsulphonium N-phosphonomethylglycine and sodium sesqui-N-phosphonomethylglycine. Combinations of two or more PMCM compounds can be employed in the composition formulation and methods of the present invention.

[0060] The following examples are illustrative of the present invention. All amounts are by weight unless otherwise indicated.

PATENT COOPERATION TREATY

WO 2004/100661
PCT/US2004/014

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Applicant

ICI AMERICAS, INC. et al

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Mayer, Brown, Rowe & Maw LLP

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7/2**[0061] Example 1**

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	44.12
b	High Fructose Corn Syrup solution	29.41
c	Ethoxylated tallowamine	26.47

[0062] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0063] Example 2

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	46.15
b	High Fructose Corn Syrup	15.38
c	Ethoxylated tallowamine	30.77
d	C ₉ -C ₁₁ alkylpolysaccharide	7.69

[0064] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0065] Example 3

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	45.45
b	High Fructose Corn Syrup solution	18.16
c	Ethoxylated tallowamine	30.30
e	Dodecylbenzenesulfonate, isopropylamine salt	6.06

[0066] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0067] Example 4

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	42.55
b	High Fructose Corn Syrup solution	25.55
c	Ethoxylated tallowamine	28.37
f	Sorbitan monooleate	3.55

[0068] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0069] Example 5

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	44.12
b	High Fructose Corn Syrup solution	14.71
c	Ethoxylated tallowamine	29.41
d	C ₉ -C ₁₁ alkylpolysaccharide	8.82
f	Mono- and di-glycerides	2.94

[0070] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0071] Example 6

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	43.17
b	High Fructose Corn Syrup solution	18.71

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c	Ethoxylated tallowamine	28.78
e	Dodecylbenzenesulfonate, isopropylamine salt	7.19
f	Sorbitan monooleate	2.16

[0072] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0073] Example 7

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	33.78
b	High Fructose Corn Syrup solution	14.93
c	Ethoxylated tallowamine	29.85
d	C ₉ -C ₁₁ alkylpolysaccharide	7.46
e	Dodecylbenzenesulfonate, isopropylamine salt	2.99

[0074] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0075] Example 8

The following concentrate is prepared:

<u>Component code</u>	<u>Component Name</u>	<u>Wt. Amount</u>
a	Mineral oil	37.97
b	High Fructose Corn Syrup solution	25.32
c	Ethoxylated tallowamine	25.32
d	C ₉ -C ₁₁ alkylpolysaccharide	6.33
e	Dodecylbenzenesulfonate, isopropylamine salt	2.53
f	Sorbitan monooleate	2.53

[0076] The foregoing concentrate self-emulsifies upon 5% dilution in water. When 0.5% (v/v) parts of the agrochemical glyphosate is incorporated into the concentrate prior to dilution in water the diluted composition is effective as a herbicide.

[0077] One skilled in the art will appreciate that the present invention can be practiced by other than the described embodiments that are presented for purposes of illustration and not of limitation

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5. The composition claimed in claim 4 wherein each of components d, e, and f are present.

6. The composition as claimed in claim 4 in which in the concentrate composition the relative weight proportions of the components are as follows:

- a) about 25 to about 75,
- b) about 15 to about 45,
- c) about 5 to about 60,

and at least one of component d, e, or f is present in an amount of

- d) about 2 to about 15,
- e) about 2 to about 15,
- f) about 2 to about 15.

7. The composition as claimed in claim 6 in which in the concentrate composition the relative weight proportions of the components are as follows:

- a) about 30 to about 60,
- b) about 20 to about 45,
- c) about 10 to about 45,

and at least one of component d, e, or f is present in an amount of

- d) about 3 to about 15,
- e) about 3 to about 15,
- f) about 3 to about 15.

8. A composition as claimed in claim 2 wherein said oil component a of said concentrate composition has a boiling point of over 200° C.

9. A composition as claimed in claim 2 wherein said oil component a of said concentrate composition comprises a mineral oil, a vegetable oil, an ester of a C₄-C₂₂ fatty acid, or a mixture of more than one of these.

10. A composition as claimed in claim 2 wherein said non-surfactant saccharide b is selected from the group consisting of a monosaccharide, an oligosaccharide and a polysaccharide.

Claims:

1. A homogeneous and self-emulsifying oil-based agrochemical concentrate composition which comprises:
 - a) at least one oil component;
 - b) at least one non-surfactant saccharide; and
 - c) about 0.5% to about 50% by weight of at least one surfactant;wherein the weight ratio of said oil to said non-surfactant saccharide is between about 1:100 to about 100:1.
2. The homogeneous composition claimed in claim 1 wherein said at least one of surfactant c. is non-ionic.
3. The homogeneous composition as claimed in claim 2 which comprises:
 - a) from about 10 to about 90 parts by weight of said at least one oil component;
 - b) from about 10 to about 90 parts by weight of said at least one non-surfactant saccharide, present in solution; and
 - c) from about 5 to about 80 parts by weight of said at least one non-ionic surfactant.
4. The homogeneous composition as claimed in claim 1 which comprises
 - a) from about 10 to about 90 parts by weight of at least one oil component;
 - b) from about 10 to about 90 parts by weight of at least one non-surfactant saccharide solution; and
 - c) from about 5 to about 80 parts by weight of at least one non-ionic surfactant; and which further comprises at least one of the following additional components:
 - d) from about 1 to about 20 parts by weight of at least one surfactant hydrocarbyl saccharide; or
 - e) from about 1 to about 20 parts by weight of at least one anionic surfactant; or
 - f) from about 1 to about 20 parts by weight of at least one additional non-ionic surfactant.

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11. A composition as claimed in claim 2 wherein said non-ionic surfactant c has the formula:



wherein:

R^1 is a hydrocarbyl, hydrocarbonyl, or hydrocarbamidyl group, which suitably contains from 6 to 24, preferably 8 to 22, and especially 12 to 18 carbon atoms, a glycerol or polyglycerol group, or a sorbitan or sorbitol group;

A is a polyalkylene oxide unit containing an average of n alkylene oxide groups or mixed alkylene oxide groups, where the alkylene groups each have 2 to 8, preferably 2 or 3, carbon atoms;

n is between 0 and 40, preferably between 2 and 30, and most preferably between 5 and 20;

R^2 is hydrogen or hydrocarbonyl residue having 8 to 22 carbon atoms, or a polycarboxylic acid residue having 2 to 6 carbon atoms such as malate, fumarate, maleate, succinate, or citrate, or an oligomer thereof;

R^3 is a hydrocarbyl or hydrocarbonyl group having 8 to 22 carbon atoms, preferably 12 to 18.

12. A composition as claimed in claim 9 wherein said oil component a is present in amount of about 30 to about 60 parts by weight and about 15 to about 45 parts by weight of total surfactant is present.

13. A composition as claimed in claim 11 wherein said non-ionic surfactant c is selected from the group consisting of alkoxylated fatty acids, polyalkylene glycol esters, alkoxylated glycerides, alkoxylated sorbitan and sorbitol esters, alkylphenol alkoxylates, alcohol alkoxylates, alkylamine alkoxylates, alkanolamides and alkoxylated alkanolamides.

14. A composition as claimed in claim 4 wherein at least one of said components d, e, or f is present and said component d has the formula:



wherein:

- R is a hydrophobic moiety;
 G is a saccharide residue; and
 a has an average value of at least 1.

and said component e. has the formula:



wherein:

R¹ is a hydrocarbyl group having 6 to 24 carbon atoms, preferably 8 to 22 carbon atoms, and most preferably 12 to 18 carbon atoms;

A is a polyalkylene oxide unit containing an average of n alkylene oxide groups or mixed alkylene oxide groups, where the alkylene groups each have 2 to 8, preferably 2 or 3, carbon atoms;

n is between 0 and 60, especially between 2 and 30, and preferably between 5 and 20;

X is a group including at least one acidic H atom or salt thereof

and said component f. has the formula:



wherein:

R¹ is a hydrocarbyl, hydrocarbonyl, or hydrocarbamidyl group, which suitably contains from 6 to 24, preferably 8 to 22, and especially 12 to 18 carbon atoms, a glycerol or polyglycerol group, or a sorbitan or sorbitol group;

A is a polyalkylene oxide unit containing an average of n alkylene oxide groups or mixed alkylene oxide groups, where the alkylene groups each have 2 to 8, preferably 2 or 3, carbon atoms;

n is between 0 and 40, preferably between 2 and 30, and most preferably between 5 and 20;

R² is hydrogen or a hydrocarbonyl group having 8 to 22 carbon atoms, or a polycarboxylic acid residue having 2 to 6 carbon atoms such as malate, fumarate, maleate, succinate, or citrate, or an oligomer thereof;

R³ is a hydrocarbyl or hydrocarbonyl group having 8 to 22 carbon atoms, preferably 12 to 18.

15. A composition as claimed in claim 14 wherein component d is present as an alkyl polyglucoside of the general formula:



where n is from 8 to 14 and b is greater than or equal to one and less than three.

16. A composition as claimed in claim 14 wherein component e. is selected from is selected from the group consisting of alkyl carboxylates and alkyl ether carboxylates, alkyl sulfates and alkyl or alkylphenyl ether sulfates, alkyl or alkylphenyl phosphates and alkyl or alkylphenyl ether phosphates, alkyl or alkylphenyl sulfosuccinates and alkyl or alkylphenyl ether sulfosuccinates, alkyl or alkylphenyl sulfonates, and alkyl or alkylphenyl phosphonates.

17. A composition as claimed in claim 14 wherein component f is selected from the group consisting of glycerol or polyglycerol esters, sorbitol or sorbitan esters, ethylene or propylene glycol esters, polyethylene glycol esters, or fatty alcohols.

18. A method of use for the composition in claim 2 wherein said concentrate is emulsified on dilution into water and the diluted formulation additionally comprises an agrochemical.

19. A method of use for the composition in claim 2 wherein said concentrate is emulsified on dilution into water and the agrochemical is a herbicide, either selective or nonselective.

20. A method of use for the composition in claim 2 wherein said concentrate is emulsified on dilution into water and the agrochemical is one or more growth regulators, herbicides, and/or pesticides.

21. A method as claimed in claim 18 in which the amount water used to dilute the concentrate is from 10 to 10,000 times the weight of the concentrate composition.

22. A method of treating vegetation by applying to plants and/or soil a diluted formulation made as claimed in claim 19.

23. A method as described in claim 19 wherein the agrochemical is at least one phosphonomethyl-N-carboxymethyl herbicides of the formula:



wherein:

each R^1 is independently halogen, -NHOH, -N(R²)₂, -OR³, -SR³ or -OM,

where R^2 is independently a hydrogen, or alkyl or hydroxyalkyl, alkenyl or phenyl;

each R^3 is independently hydrogen, alkyl, hydroxyalkyl or chloroalkyl, alkoxy, alkylene amine, phenyl or benzyl;

M is hydrogen or an agriculturally acceptable salt forming moieties such as alkali metal, alkaline earth metal, stannic, ammonium, organic ammonium, alkyl sulfonium, alkyl sulfoxonium, alkyl phosphonium moieties or combinations thereof; and Z is hydrogen, an organic moiety or an inorganic moiety.

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ARGENTINA
UOI 50282-AR

MEMORIA DESCRIPTIVA

Sobre :

SISTEMAS HOMOGENEOS A BASE DE SACARIDO LIQUIDO Y ACEITE

Solicitante : ICI Americas Inc.

Residencia : 10 Finderne Avenue, Bridgewater, New Jersey 08807, USA

SISTEMAS HOMOGENEOS A BASE DE SACARIDO LIQUIDO Y ACETE**Antecedentes de la invención**

[0001] Las composiciones agroquímicas han sido utilizadas para mejorar la calidad y cantidad de productos agrícolas. A este respecto, tales composiciones pueden realzar la actividad biológica y actuar como nutrientes, reguladores del crecimiento y/o pesticidas, por ejemplo como herbicidas, insecticidas, fungicidas o acaricidas. Sin embargo, dado que tales composiciones son costosas de producir y adquirir, en la práctica sería deseable reducir su coste general por el hecho de mejorar su eficacia por unidad de área tratada con el producto agroquímico.

[0002] Al objeto de mejorar o realzar la eficacia de muchos productos agroquímicos, se añaden ciertos materiales a las mezclas de pulverización agrícolas de base acuosa que contienen el producto agroquímico, para aplicarse entonces de forma simultánea a los sustratos agrícolas. Dichos materiales son identificados generalmente como adyuvantes de pulverización agrícolas y existen en una amplia variedad de formas y composiciones que se utilizan hoy día en agricultura comercial. Dichos productos adyuvantes se emplean, en su uso habitual, para proporcionar un amplio conjunto de efectos, incluyendo, pero no de forma limitativa, el control del espumado, el aumento de la eficacia de un producto agroquímico específico y/o la modificación de la mezcla de pulverización agrícola respecto a una estabilidad o modulación mejorada del diámetro de las gotitas pulverizadas.

[0003] En los Estados Unidos, la mayoría de los productos adyuvantes convenientes desde el punto de vista económico, empleados para mejorar o realzar la eficacia de un producto agrícola, principalmente un pesticida, se suministran como líquidos. Los productos adyuvantes líquidos preferidos (tanto por conveniencia como por economía) producidos y comercializados en los Estados Unidos, se suministran como líquidos

concentrados y pertenecen a dos categorías principales. Dichas categorías son: (1) composiciones de aceites y surfactantes auto-emulsionantes identificadas más comúnmente como Concentrados de Aceites Agrícolas (COC) y (2) formulaciones de surfactantes fácilmente solubles o dispersables en agua conocidas como Surfactantes No Iónicos (NIS) líquidos. Los canales de distribución comercial en los Estados Unidos transportan de un modo eficaz grandes volúmenes de tales productos, principalmente a granel, haciendo que los productos de tipo COC y NIS resulten muy económicos para el uso al cual están destinados. Al mejorar la eficacia de los pesticidas más costosos por medio de su combinación en las mezclas a pulverizar con un producto adyuvante económicamente ventajoso y fundamentalmente de bajo costo, se puede mejorar la economía global de la agricultura comercial. De esta manera, el uso de productos adyuvantes eficaces disminuye el costo de temporada para producir productos agrícolas y también puede mejorar la producción de tales productos, ofreciendo con ello ventajas económicas a quienes lo utilizan.

[0004] Uno de los grupos individuales más grandes de tales productos adyuvantes líquidos eficaces, comercializados en los Estados Unidos (en volumen), consiste en una composición COC que contiene entre 60 y 90% de una calidad agrícola adecuada de aceite mineral; una forma alternativa a este tipo de adyuvante contiene un aceite vegetal o un aceite de semillas metilado. Todas las formas comercialmente importantes de este tipo de adyuvante contienen habitualmente una composición emulsionante soluble en aceite constituida por una mezcla de surfactantes aniónicos y/o no iónicos que da lugar a la auto-emulsificación del componente de aceite tras la dilución en una mezcla de pulverización agrícola de base acuosa; la concentración total de surfactante en un producto COC típico puede oscilar entre 1 y 40%, muy habitualmente entre 10 y 17%.

[0005] Si bien la composición de aceite y surfactante en un producto adyuvante COC

podría ofrecerse también como un sistema pre-emulsionado en agua (una emulsión de aceite en agua), el coste añadido de producción de un producto adyuvante emulsionado tiende a convertirlo en menos ventajoso económicamente que el volumen equivalente de adyuvante de aceite ofrecido como un COC. Los sistemas a base de agua tienen también las características indeseables de ser en general más complicados de desarrollar y producir y de requerir el uso por separado de sistemas de espesado, conservación y anti-congelación debido a la tendencia de las emulsiones de base acuosa a sustentar el crecimiento microbiano, a la formación de crema o a decantar/sedimentar, tendiendo también a deteriorarse en el transcurso del tiempo o durante el ciclo de congelación-descongelación. El efecto de incluir agua como el medio dispersante diluye también a los componentes activos (composición de aceite y surfactante) haciendo con ello que el sistema sea más costoso de suministrar en el campo tomando como base una libra de adyuvante "activo". Sobre esta misma base, también aumentan los costes logísticos dado que se transporta más agua de la que puede estar presente de otro modo en un sistema de tipo COC comparable.

[0006] En los últimos tiempos, han surgido mejoras específicas con respecto a la efectividad económica de los concentrados de aceites agrícolas económicamente ventajosos hasta ahora descritos. La mayoría de estas mejoras se han centrado en dos aspectos de la composición. El primer aspecto reside en el incremento de la concentración total de emulsionante surfactante soluble en aceite, lo cual se ha traducido en un cambio de la concentración preferida de surfactante desde 12-17% hace diez años hasta aproximadamente 40% en la actualidad; este cambio se asoció con una reducción en la cantidad de producto adyuvante COC aplicado por unidad de área y se tradujo en atributos mejorados de coste en la práctica para el adyuvante. El segundo aspecto reside en la selección de tipos específicos de surfactantes tomando como base datos obtenidos

en el campo y la propia evaluación científica; este cambio se asoció con un comportamiento mejorado del producto adyuvante con productos pesticidas específicos. La publicación PCT WO 95 03881 de Auda et al. describe un concentrado agroquímico de aceite agrícola que contiene un aceite o aceites, un surfactante de sacárido hidrocarbílico y un surfactante no iónico adicional, cuyo concentrado se emulsiona fácilmente tras la dilución en agua. Dicha composición adyuvante COC se asoció con un aumento o mejora en el comportamiento de control de malas hierbas en combinación con sales solubles de N-fosfonometilglicina.

[0007] Más recientemente, la US 5,945,377 de Penner ha descrito composiciones que incorporan un herbicida para aplicarse después del brote y un monosacárido, en particular fructosa, como un potenciador del herbicida contra malas hierbas sin hacer descender la tolerancia de una planta de cultivo al herbicida. Las composiciones se emplean como una pulverización en agua en un método para destruir malas hierbas. Aunque no es considerado como un adyuvante NIS, se evaluó el jarabe de maíz como un adyuvante con varios herbicidas aplicables después del brote, en estudios tanto en invernadero como en el campo. El aumento más pronunciado de actividad herbicida se observó con la aplicación de jarabe de maíz de alto contenido en fructosa en combinación con un sulfato amónico y un adyuvante no iónico eficaz con herbicidas aniónicos tales como glifosato y glufosinato para el control de especies de gramíneas tal como cola de zorra gigante. La eficacia del jarabe de maíz como adyuvante fue específica tanto hacia las malas hierbas como hacia el herbicida.

[0008] La publicación anteriormente mencionada (WO 95 03881) describe surfactantes de alquilpolisacáridos auto-dispersantes en concentrados de aceites agrícolas (COC's). Estas composiciones no incluían componentes de polisacáridos no surfactantes líquidos acuosos adicionales que, según se había comprobado recientemente, promovían la

actividad herbicida del glifosato. Se llegó a la conclusión de que una composición robusta de una sola fase que contiene: (1) un aceite adyuvante, (2) un sacárido adyuvante y (3) una cantidad óptima de surfactante con una cantidad mínima correspondiente de agua adicional podía permitir el suministro de un producto adyuvante agrícola líquido altamente concentrado con una concentración total de surfactante similar a la utilizada hoy día (alrededor de 10-40% p/p). La incorporación con éxito del sacárido adyuvante económico y eficaz mejoraría la efectividad económica del producto adyuvante acabado. El producto resultante resulta comercialmente ventajoso para el fabricante y económicamente beneficioso para el comprador/usuario. Otra ventaja derivada de la combinación de la composición adyuvante de sacárido y surfactante con la composición adyuvante COC tradicional sería la importante ventaja comercial obtenida al poder proporcionar una composición adyuvante eficaz en términos muy amplios que tiene las características preferidas de los productos COC, NIS y de los tipos de sacáridos adyuvantes más recientes.

[0009] Las composiciones descritas están destinadas a ser alternativas comerciales a los adyuvantes COC tradicionales basados en 17 y 40% de surfactante en aceite, utilizados en el mercado agrícola. Estos tipos de adyuvantes COC, si bien son eficaces económicamente para utilizarse con la mayoría de los productos agroquímicos dispersables en agua, no constituyen el tipo más eficaz de adyuvante para las sales solubles de N-fosfonometilglicina, conocidas más comúnmente como glifosato, el cual representa el pesticida comercial más grande comercializado en los Estados Unidos y que, como resultado, presenta la oportunidad más grande en lo que se refiere a sales adyuvantes individuales. La mayor parte de los adyuvantes NIS eficaces para utilizarse con glifosato, identificados como alquil(sebo)aminas etoxiladas, son en la actualidad habitualmente combinados para formar productos de glifosato en solución concentrada

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y, por tanto, no son fácilmente accesibles a productos adyuvantes destinados a combinarse en mezclas de pulverización agrícolas. Con el término de la vida legal de patentes sobre productos en solución concentrada de sal de glifosato, puede también llegar a disponerse de otras formas del pesticida, incluyendo productos que de manera intencionada no incluyen el adyuvante NIS preferido como un medio para reducir el coste del glifosato formulado y aumentar su concentración en productos en solución. Serían ventajoso alterar el producto COC tradicional o el producto COC descrito en WO 95 03881 para demostrar un aumento mejorado de la eficacia con productos de glifosato; esto resultaría sumamente conveniente como un medio para expansionar el mercado para el producto adyuvante COC altamente efectivo en cuanto a coste.

[0010] Idealmente, sería deseable conseguir una composición surfactante que sirva, en combinación, como el auto-emulsionante del adyuvante COC y como compatibilizante/estabilizante para el componente de sacárido y que tenga también la capacidad de estabilizar y auto-emulsionar el aceite únicamente (sin el componente de sacárido) y que al mismo tiempo presente ventajas especiales al ofrecer una economía mejorada en la compra de una sola composición surfactante y al permitir la producción flexible de adyuvantes COC en la misma composición surfactante con y sin componentes de sacáridos líquidos añadidos. Dado que el adyuvante de jarabe de maíz requiere también la aplicación simultánea de un adyuvante de surfactante no iónico para lograr un comportamiento óptimo, la combinación directa del aceite y del jarabe de maíz con un único sistema surfactante que "activara" al sacárido y que al mismo tiempo emulsionara al componente de aceite, representaría las ventajas económicas y competitivas más grandes. Esencialmente, al utilizar el concepto de producto combinado COC y NIS de sacárido, la composición sería 100% activa con una concentración total mínima de la composición surfactante requerida para lograr el comportamiento óptimo.

Puesto que el surfactante constituye la partida más costosa en la producción en base al precio de adquisición (por libra) del componente, sería altamente deseable reducir el surfactante a la cantidad mínima requerida para lograr la actividad óptima.

[0011] La mayor dificultad en el desarrollo del producto adyuvante COC combinado de sacárido consiste en la identificación de sistemas surfactantes adecuados que permitan la formulación de composiciones homogéneas que funcionen como estabilizantes potentes para una solución de sacárido líquido altamente concentrada en un aceite adyuvante y que den lugar a la auto-emulsificación tras la dilución que sea necesaria. Estos dos efectos opuestos han de ser desarrollados en un producto adyuvante con un mínimo de surfactante total. Preferentemente, en la composición deberá incluirse también un agente controlador del espumado.

[0012] En la US 5.885.646 de Wong se describe un procedimiento para la preparación de una crema de nueces que tiene un nivel de azúcar de alrededor de 15 a 50% y en especial para la preparación de una crema de nueces aromatizada que tiene dichos niveles de azúcar relativamente elevados. Se prepara una mezcla sustancialmente homogénea a partir de una suspensión fluida que consiste esencialmente en una mezcla íntima de azúcar, aceite líquido y lecitina como surfactante para mejorar la fluidez de la suspensión, una mezcla que contiene sólidos de nueces y un aromatizante que preferentemente se añade a la suspensión fluida. La crema de nueces aromatizada resultante es más fluida y más blanda que los productos preparados sin utilizar la suspensión fluida. Esta invención no proporciona las características de homogeneidad o auto-emulsificación de productos líquidos y ofrece una viscosidad relativamente alta, lo cual resulta irrelevante para esta invención.

[0013] En la US 3.959.498 de Lyall se describe un procedimiento en una etapa para aplicar azúcar y una grasa o aceite comestible a bases de cereales. No es necesario

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realizar una etapa separada para pulverizar el aceite en el sustrato de cereal. La invención proporciona igualmente un revestimiento en emulsión de los cereales para conseguir la finalidad anterior, así como un método de preparación de dicho revestimiento. A una solución acuosa de azúcar (60-85% de sólidos) se añade una cantidad de grasas o aceites comestibles u otro material oleaginoso derivado de aceites o grasas comestibles (5-32%) junto con una cantidad de emulsionante (0,5-5%), para preparar una emulsión de jarabe que tiene un contenido en agua del orden de 9-34% en peso. La grasa o aceite comestible y el emulsionante se añaden al jarabe acuoso a una temperatura del orden de 115° F a 155° C (46,1° C a 68,3° C), y después de la emulsificación, la mezcla se calienta a una temperatura de alrededor de 180° F (82,2° C). Como en el ejemplo anterior, esta invención no proporciona las características de homogeneidad o auto-emulsificación de un producto líquido y demuestra una viscosidad relativamente alta, lo cual hace que resulte inaplicable en esta invención. Además, proporciona una emulsión de aceite en agua, mientras que la composición aquí reivindicada es un producto líquido homogéneo (solución o microemulsión).

Resumen de la invención

[0014] La presente invención implica el desarrollo de sistemas estables en frío (0° C), a temperatura ambiente (alrededor de 20-25° C) y en caliente (por ejemplo, alrededor de 50° C) que comprenden mezclas de un producto de sacárido líquido concentrado con un aceite de pulverización agrícola. Estas mezclas siguen siendo líquidos homogéneos en el intervalo de temperatura de alrededor de 0-50° C y son auto-dispersantes tras la dilución en aceite. Los líquidos homogéneos descritos contienen cantidades de 0,5-50% en peso de surfactante, con relaciones de aceite:producto de sacárido comprendidas entre 1:100 y 100:1, presentándose la composición preferida entre 1:10 y 10:1, más preferentemente entre 1:3 y 3:1 y muy especialmente entre 1:2 y 2:1.

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[0015] La invención comprende los siguientes componentes básicos: un aceite biológicamente eficaz, un producto de sacárido líquido (consistente principalmente en jarabes viscosos concentrados a base de agua) y uno o más surfactantes para aportar un sistema de suministro (solución o microemulsión) homogéneo, estable y dispersable en agua para adyuvantes agrícolas. En general no se requiere una composición surfactante o tipo químico de surfactante específico; en base al entendimiento de las interacciones que han sido desarrolladas, se preparó una amplia variedad de composiciones surfactantes capaces de suministrar el producto descrito.

[0016] Las composiciones surfactantes empleadas para desarrollar dichas formulaciones incluyen, pero no de forma limitativa, alquilpolisacáridos, ésteres de fosfatos, ésteres de sorbitan, mono- y diglicéridos, polisorbatos y alquilaminas etoxiladas. Se pueden emplear cantidades menores de agua para conseguir la compatibilización de los sistemas de aceite:surfactante:sacárido; en ningún caso se añadió más de 25% de agua para conseguir la compatibilización. Los sistemas surfactantes que dan lugar a las características deseadas de homogeneidad y compatibilidad se emplearon normalmente en una cantidad de 10-40%, conteniendo las composiciones más preferidas de 10 a 35%; y conteniendo las composiciones sumamente preferidas de 10 a 25%.

[0017] Preferentemente, el surfactante incluye un surfactante no iónico y con suma preferencia consiste fundamentalmente en uno o más surfactantes no iónicos. Si se desea, pueden emplearse otros surfactantes, tal como al menos un surfactante aniónico, por ejemplo una sal aniónica de alcanolamina.

[0018] Esta invención se refiere a composiciones surfactantes y, en particular, a composiciones que contienen una pluralidad de surfactantes y al menos un aceite, y que son fácilmente emulsionables en agua.

[0019] La invención proporciona una composición de concentrado que comprende:

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- a al menos un componente de aceite;
- b al menos un sacárido no surfactante;
- c al menos un surfactante no iónico.

[0020] La composición puede comprender también al menos uno de los siguientes componentes:

- d al menos un hidrocarbilo sacárido surfactante; o
- e al menos un surfactante aniónico; o
- f al menos otro surfactante no iónico soluble en aceite.

Descripción detallada de la invención

[0021] La composición de la invención asume habitualmente la forma de un concentrado a base de aceite que es homogéneo durante al menos 24 horas y que emulsifica fácilmente tras la dilución en agua. Se utilizará como un precursor para la dilución con agua para mezclas de pulverización agrícolas que contienen un producto agroquímico. Dichas mezclas de pulverización contendrán uno o más ingredientes y/o nutrientes con actividad pesticida.

[0022] La composición de concentrado puede comprender también un líquido miscible en agua, el cual puede ser conveniente en el caso de que la viscosidad de la composición fuese de otro modo inconvenientemente alta. Dicho líquido puede incluir agua o puede consistir en agua. El contenido en agua es con preferencia lo suficientemente bajo para que la composición permanezca homogénea durante al menos 24 horas después de ser preparada. Los componentes y sus proporciones se eligen preferentemente de manera que cuando cualquiera de los componentes resulten fácilmente disponibles únicamente como soluciones acuosas, tal como HFCS (jarabe de maíz de alto contenido en fructosa), la composición obtenida mediante la mezcla de sus componentes sea estable, independientemente del agua que se introduzca con ello. Cuando la composición de

concentrado incluye agua, el concentrado será normalmente una solución del agua en el aceite, actuando la combinación surfactante para solubilizar el agua, o como una emulsión coloidal de agua en aceite o como una microemulsión en donde el agua se dispersa en forma de gotitas muy diminutas, de manera que la composición resulte clara o transparente.

[0023] El componente de aceite tiene habitualmente un punto de ebullición por encima de alrededor de 200° C a presión atmosférica y un punto de fusión no mayor de alrededor de 60° C. Puede comprender, por ejemplo, un aceite mineral, un aceite vegetal opcionalmente hidrogenado, tal como aceite de algodón, aceite de linaza, aceite de mostaza, aceite de *Nilia indica*, aceite de semillas negras, aceite de *Clarisia racemosa*, aceite de oliva, aceite de palma, aceite de pepitas de palma, aceite de cacahuete, aceite de perilla, aceite de amapolas, aceite de colza, aceite de cártamo, aceite de sésamo o aceite de soja, así como un éster (especialmente un éster C₁ a C₆) de un ácido graso C₂ a C₂₂ (especialmente un ácido graso C₁₂ a C₁₈), por ejemplo, laurato, miristato, palmitato, palmitoleato, linoleato, linolenolato, estearato u oleato de metilo, etilo o propilo, o una mezcla de los anteriores, por ejemplo, un éster en donde el número total de átomos de carbono en la molécula no excede de 20, y preferentemente un éster de un ácido graso C₁₂ a C₁₈, por ejemplo, laurato de metilo, etilo o propilo, o una mezcla de los mismos.

[0024] El componente de aceite preferentemente también contiene o está asociado con al menos un surfactante soluble en aceite, especialmente uno que puede hacer que el aceite sea auto-emulsionable en agua. Dicho surfactante puede incluir al menos uno de un valor HLB (equilibrio hidrófilo-lipófilo) relativamente alto en combinación con uno de bajo valor HLB, por ejemplo estearato de calcio. Dicho componente de solución de aceite puede encontrarse en forma del así llamado "aceite agrícola" o "adyuvante de aceite" comercialmente disponible. Un componente de aceite típico contiene alrededor

de 99 a 45, con preferencia alrededor de 90 a 60, partes en peso de aceite, y alrededor de 1 a 55, con preferencia alrededor de 10 a 40, partes en peso de uno o más surfactantes solubles en aceite. Cuando está presente agua en forma solubilizada o como una emulsión coloidal o una microemulsión, el surfactante soluble en aceite puede estar distribuido entre la fase oleosa y las fases acuosas (o puede estar presente en la interfase).

[0025] La solución de sacárido líquido puede ser de un monosacárido, oligosacárido o un polisacárido o una mezcla de los mismos; los sacáridos pueden ser de naturaleza lineal, ramificada o cíclica. Para dichas soluciones de sacáridos líquidos, el disolvente puede ser agua, propilenglicol o glicerol o cualquier combinación de los mismos. Resulta común referirse a las soluciones de sacáridos líquidos como jarabes. Los oligosacáridos presentes en solución son normalmente identificados como maltodextrinas, mientras que los polisacáridos son generalmente identificados como dextrinas. Entre las soluciones de sacáridos líquidos, los compuestos de uso particular en esta invención incluyen compuestos y mezclas de compuestos descritos como HFCS, jarabe de maíz, edulcorante de maíz, azúcar invertido, jarabe de azúcar invertido, azúcar, jarabe de azúcar y maltodextrinas en donde la solución de sacárido líquido resultante es homogénea y estable durante al menos 24 horas y contiene alrededor de 75 partes en peso de agua o menos, con preferencia alrededor de 15 a 50 partes en peso de agua.

[0026] Es conveniente que cuando el sacárido es un oligosacárido el mismo tenga la fórmula general:



en donde n es mayor de o igual a 1 y no mayor de 50. En particular, el sacárido puede ser uno en donde el valor medio de n es generalmente de al menos 1 y no mayor de 5.

Un material particularmente útil de este tipo es aquel en donde n tiene un valor medio de

aproximadamente 1 y en donde el sacárido es un monosacárido y el monosacárido es un ceto-azúcar, más preferentemente fructosa. La fructosa es comercialmente disponible como HFCS y se puede utilizar satisfactoriamente el material designado, por ejemplo, como IsoClear 55 por Cargill.

[0027] El surfactante o los surfactantes no iónicos pueden ser cualesquiera que proporcionen una composición que sea estable y homogénea durante al menos 24 horas después de su preparación.

[0028] Los surfactantes no iónicos preferidos son de fórmula:



en donde

R^1 es un grupo hidrocarbilo, hidrocarbonilo o hidrocarbamidilo, que adecuadamente contiene de 6 a 24, con preferencia de 8 a 22 y especialmente de 12 a 18 átomos de carbono, un grupo glicerol o poliglicerol o un grupo sorbitan o sorbitol;

A es una unidad de óxido de polialquileño que contiene una media de n grupos de óxido de alquileño o de grupos de óxido de alquileño mixtos, en donde los grupos alquileño tienen cada uno de 2 a 8, preferentemente 2 o 3, átomos de carbono;

n está comprendido entre 0 y 40, preferentemente entre 2 y 30 y más preferentemente entre 5 y 20;

R^2 es hidrógeno o un residuo hidrocarbonilo que tiene de 8 a 22 átomos de carbono, o un residuo de ácido policarboxílico que tiene de 2 a 6 átomos de carbono, tal como malato, fumarato, maleato, succinato o citrato, o un oligómero de los mismos;

R^3 es un grupo hidrocarbilo o hidrocarbonilo que tiene de 8 a 22 átomos de carbono,

preferentemente de 12 a 18.

[0029] El hidrocarbilo sacárido surfactante puede ser cualquiera que proporcione una composición que sea estable y homogénea durante al menos 24 horas después de su preparación.

[0030] El hidrocarbilo sacárido surfactante puede ser un monoglicósido o un poliglicósido o una mezcla de los mismos. Es común referirse a los hidrocarbilo sacáridos surfactantes como hidrocarbilo polisacáridos incluso cuando la mitad de sacárido solo contiene una unidad de sacárido. Normalmente, dichos surfactantes son mezclas de compuestos con unidades de monosacárido y polisacárido (incluyendo disacárido). Entre los glicósidos, los compuestos de uso particular en esta invención incluyen compuestos y mezclas de compuestos de fórmula:



en donde

R es una mitad hidrófoba;

G es un residuo de sacárido; y

a tiene un valor medio de al menos 1.

[0031] El grupo R puede ser un grupo hidrocarbilo opcionalmente sustituido. En particular, R puede ser un grupo alquilo, cicloalquilo, arilo, alcarilo, aralquilo o alquenilo y preferentemente es un grupo alquilo. El grupo R contiene adecuadamente de 4 a 30 átomos de carbono, con preferencia hasta 24 átomos de carbono, más preferentemente de 6 a 18 átomos de carbono y en especial de 8 a 14 átomos de carbono. De este modo, R puede ser una mezcla de grupos alquilo o alcoxi que contienen, en promedio, por ejemplo de 8 a 14 átomos de carbono.

[0032] El residuo de sacárido G puede derivarse de uno o más de fructosa, glucosa, manosa, galactosa, telosa, gulosa, alosa, altrosa, idosa, arabinosa, xilosa, lixosa y ribosa

o de mezclas de los mismos. El grupo G se deriva convenientemente de unidades de glucosa y el glicósido es entonces un glucósido. Si se deriva de sucrosa, los grupos comprenderán residuos de fructosa y glucosa.

[0033] El valor de a es el grado de polimerización. Habitualmente tiene un valor medio de al menos 1,1, con preferencia de al menos 1,2 y en especial de al menos 1,3. El valor de a generalmente no es mayor de 8 y con preferencia no es mayor de 4, por ejemplo no es mayor de 2. Cuando el glicósido es un alquil glucósido, el valor de a se encuentra convenientemente entre 1 y 2.

[0034] Se obtienen resultados convenientes cuando el glicósido es un alquil poliglucósido de fórmula general:



en donde

n es de 8 a 14 y

b es mayor de 1 y no mayor de 2.

[0035] En particular, el glucósido puede ser uno en donde el valor medio de n es de 9 a 13 y en especial de alrededor de 10. El valor de b es normalmente de al menos 1,3 y no mayor de 1,9. Un material de este tipo particularmente útil es aquel en donde n es de 8 a 11 y tiene un valor medio de 10 y b es 1,35 aproximadamente. Los hidrocarbilo sacáridos surfactantes son comercialmente disponibles y se pueden emplear satisfactoriamente los materiales designados, por ejemplo, como Atplus 452 y Atplus 438 por Uniqema o comercializados con el nombre registrado Triton BG 10 por Dow Chemicals.

[0036] El surfactante o los surfactantes aniónicos pueden ser cualesquiera que proporcionen una composición que sea estable y homogénea durante al menos 24 horas después de su preparación.

[0037] El surfactante o los surfactantes aniónicos pueden ser cualesquiera que

proporcionen una composición que sea estable y homogénea durante al menos 24 horas después de su preparación. Los mismos son caracterizados como al menos un compuesto surfactante aniónico de fórmula general:



en donde

R¹ es un grupo hidrocarbilo que tiene de 6 a 24 átomos de carbono, con preferencia de 8 a 22 átomos de carbono y más preferentemente de 12 a 18 átomos de carbono;

A es una unidad de óxido de polialquileo que contiene una media de *n* grupos de óxido de alquileo o grupos de óxido de alquileo mixtos, en donde los grupos alquileo tienen cada uno de 2 a 8, con preferencia 2 o 3, átomos de carbono;

n está comprendido entre 0 y 60, con preferencia entre 2 y 30 y más preferentemente entre 3 y 15;

X es un grupo que incluye al menos un átomo de H ácido o una sal del mismo, convenientemente una sal de amina.

[0038] En la fórmula anterior, X es un grupo que incluye al menos un átomo ácido o una sal del mismo, por lo cual se quiere dar a entender que el grupo X puede ser ionizado para formar un grupo aniónico en un medio acuoso. El grupo proporciona así una función aniónica, haciendo con ello que el surfactante sea aniónico. Esta función puede ser un grupo ácido de fósforo, azufre o carbono parcial o totalmente oxidado.

[0039] El otro surfactante no iónico o los otros surfactantes no iónicos pueden ser cualesquiera que proporcionen una composición que sea estable y homogénea durante al menos 24 horas después de su preparación.

[0040] Se obtienen en particular resultados convenientes cuando el surfactante no iónico

es de fórmula general (I) o (II):



en donde

- R¹** es un grupo hidrocarbilo, hidrocarbonilo o hidrocarbamidilo, que adecuadamente contiene de 6 a 24, con preferencia de 8 a 22 y especialmente de 12 a 18 átomos de carbono, un grupo glicerol o poliglicerol o un grupo sorbitan o sorbitol;
- A** es una unidad de óxido de polialquileno que contiene una media de n grupos de óxido de alquileno o de grupos de óxido de alquileno mixtos, en donde los grupos alquileno tienen cada uno de 2 a 8, preferentemente 2 o 3, átomos de carbono;
- n** está comprendido entre 0 y 40, preferentemente entre 2 y 30 y más preferentemente entre 5 y 20;
- R²** es hidrógeno o un residuo hidrocarbonilo que tiene de 8 a 22 átomos de carbono, o un residuo de ácido policarboxílico que tiene de 2 a 6 átomos de carbono, tal como malato, fumarato, maleato, succinato o citrato, o un oligómero de los mismos;
- R³** es un grupo hidrocarbilo o hidrocarbonilo que tiene de 8 a 22 átomos de carbono, preferentemente de 12 a 18.

[0041] Las proporciones relativas del componente de aceite (a), de la solución de sacárido líquido (b) y del surfactante no iónico (c) son adecuadamente (en peso):

- a** 10 a 90, especialmente 25 a 75, preferentemente 30 a 60,
- b** 10 a 90, especialmente 15 a 45, preferentemente 20 a 40, y
- c** 5 a 80, especialmente 5 a 60, preferentemente 10 a 45;

y las proporciones opcionalmente de al menos un hidrocarbilo sacárido surfactante (d); o

surfactante aniónico (e); o surfactante no iónico (f), son como sigue:

d 1 a 20, especialmente 2 a 15, preferentemente 3 a 10, o

e 1 a 20, especialmente 2 a 15, preferentemente 3 a 10, o

f 1 a 20, especialmente 2 a 15, preferentemente 3 a 10.

[0042] Cualquier agente químico específico para el uso al que está destinada la composición, será un compuesto agroquímico. El compuesto agroquímico consiste habitualmente en una o más sustancias nutrientes, reguladores del crecimiento, herbicidas y/o pesticidas, por ejemplo insecticidas, fungicidas o acaricidas.

[0043] La invención incluye un procedimiento para la preparación de la composición de la invención que comprende mezclar los componentes de forma conjunta.

[0044] La invención incluye además una formulación diluida que comprende una composición que incluye los componentes (a), (b) y (c) según la invención con una cantidad de agua que va desde 10 a 10.000 veces aproximadamente el peso de la composición. Las composiciones de concentrados de la invención se emulsionan fácilmente tras la dilución en agua para formar la formulación. A niveles de dilución relativamente bajos, el producto será una emulsión de aceite en agua que tiene una concentración relativamente alta de aceite. Esta emulsión intermedia puede ser entonces diluida adicionalmente con agua o con una solución o suspensión acuosa de otros componentes descritos en la formulación final.

[0045] Las formulaciones diluidas se pueden preparar de varias formas. Así, una formulación que comprende componentes distintos de (a), (b), (c) y opcionalmente uno o más componentes (d), (e) o (f) y agua, se puede preparar mezclando simplemente los componentes (a), (b), (c) y opcionalmente uno o más componentes (d), (e) o (f) con agua.

[0046] En otro aspecto, la invención proporciona un método de aplicación de una

formulación de la invención a un sustrato. Modalidades de este método incluyen un método de tratamiento de vegetación por aplicación a las plantas y/o al suelo de dicha formulación según la invención, cuya formulación comprende un agente químico específico que consiste en un compuesto agroquímico.

[0047] En esta modalidad, el compuesto agroquímico puede consistir en uno o más reguladores de crecimiento, herbicidas y/o pesticidas, por ejemplo insecticidas, fungicidas o acaricidas. Esta modalidad de la invención del método de aplicación de la formulación incluye por tanto: un método de destrucción o inhibición de la vegetación por aplicación de la formulación que comprende un agente químico específico que consiste en uno o más reguladores del crecimiento y/o herbicidas, y un método de destrucción o inhibición de plagas de las plantas por aplicación de la formulación que comprende un agente químico específico consistente en uno o más pesticidas, por ejemplo insecticidas, fungicidas o acaricidas.

[0048] En esta modalidad, el efecto del compuesto agroquímico, consistente en uno o más reguladores del crecimiento, herbicidas y/o pesticidas, por ejemplo insecticidas, fungicidas o acaricidas, puede ser potenciado por el componente de aceite y/o componente de sacárido y/o componente surfactante presentes en la composición.

[0049] Ejemplos del compuesto agroquímico que habitualmente consiste en uno o más reguladores del crecimiento, herbicidas y/o pesticidas, por ejemplo insecticidas, fungicidas o acaricidas, en particular reguladores del crecimiento, herbicidas, etc, incluyen compuestos de fosfonometil-n-carboximetil (PMCM) y compuestos relacionados de fórmula:



en donde

cada R^7 es independientemente halógeno, $-NHOH$, $-N(R^8)_2$, $-OR^9$, SR^9 o $-OM$, en donde

R⁸ es independientemente hidrógeno o alquilo o hidroxialquilo, conteniendo preferentemente menos de alrededor de 5 átomos de carbono, alquenilo, conteniendo preferentemente menos de alrededor de 5 átomos de carbono, o fenilo; cada **R⁹** es independientemente hidrógeno, alquilo, hidroxialquilo o cloroalquilo, conteniendo preferentemente menos de alrededor de 5 átomos de carbono, alcoxi, conteniendo preferentemente menos de alrededor de 5 átomos de carbono, alquilenamina, conteniendo preferentemente menos de alrededor de 12 átomos de carbono, fenilo o bencilo; **M** es hidrógeno o una mitad formadora de sales agrícolas aceptables tales como mitades de metal alcalino, metal alcalinotérreo, estánicas, amónicas, amónicas orgánicas, alquilsulfonio, alquilsulfoxonio, alquifosfonio o combinaciones de las mismas; y **Z** es hidrógeno, una mitad orgánica o una mitad inorgánica.

[0050] Patentes representativas que describen al menos algunos de tales compuestos incluyen las Patentes US 3799758, 4397676, 4140513, 4315765, 3868407, 4405531, 4481026, 4414158, 4120689, 4472189, 4341549 y 3948975. Patentes que describen compuestos PMCM en donde **Z** es distinto de hidrógeno incluyen las Patentes US 3888915, 3933946, 4062699, 4119430, 4322239 y 4084954.

[0051] En los compuestos PMCM preferidos,

Z es hidrógeno o un sustituyente orgánico;

R⁹ se elige independientemente entre hidrógeno, alquilo, hidroxialquilo o cloroalquilo, conteniendo preferentemente menos de alrededor de 5 átomos de carbono, alcoxi, conteniendo preferentemente menos de alrededor de 5 átomos de carbono, alquilenamina, conteniendo preferentemente menos de alrededor de 12 átomos de carbono, fenilo o bencilo; y

M se elige entre hidrógeno y mitades formadoras de sales agrícolas aceptables, metal alcalino, mitades fosfonio o combinaciones de las mismas.

[0052] Patentes representativas que describen al menos algunos de tales compuestos incluyen las Patentes US 3799758, 4397676, 4140513, 4315765, 3868407, 4405531, 4481026, 4414158, 4120689, 4472189, 4341549 y 3948975. Patentes que describen compuestos PMCM en donde Z es distinto de hidrógeno incluyen las Patentes US 3888915, 3933946, 4062699, 4119430, 4322239 y 4084954.

[0053] En los compuestos PMCM preferidos, Z es hidrógeno o un sustituyente orgánico tal como metilencarboxílico; metilfosfónico; y metilenciano. Otros sustituyentes orgánicos incluyen carboxilo, tal como formilo, acetilo, benzoilo, perfluoracilo y tiocarbonilo; metileno, tal como metilo ciano-, carbamoil- o carboxi-sustituido; y sustituyentes bencenosulfonilo. Patentes que describen compuestos en donde el nitrógeno tiene tres sustituyentes orgánicos incluyen las Patentes US 3455675, 3556762, 3853530, 3970695, 3988142, 3991095, 3996040, 4047927, 4180394, 4203756, 4261727 y 4312662. Un compuesto PMCM sustituido en el nitrógeno terciario es N,N-bis(fosfonometil)glicina.

[0055] Aquellos compuestos PMCM en donde Z es hidrógeno son los más preferidos cuando la fitoactividad deseada es una actividad herbicida.

[0056] Las patentes anteriormente indicadas se incorporan aquí solo con fines de referencia.

[0057] Ejemplos ilustrativos de mitades formadoras de sales agrícolamente aceptables representadas por M, como en OM, son los metales alcalinos que tienen pesos atómicos de 22 a 133 inclusive, tales como sodio, potasio o rubidio; los metales alcalinotérreos que tienen pesos atómicos de 24 a 88 inclusive, tales como magnesio o calcio; amonio y amonio alifático, en donde el grupo alifático es primario, secundario, terciario o cuaternario y preferentemente en donde el número total de átomos de carbono no excede de más de 12 aproximadamente; fenilamonio; trialkilsulfonio, preferentemente en

donde el número total de átomos de carbono en los tres sustituyentes alquilo no excede de más de seis aproximadamente, tales como trimetilsulfonio, etildimetilsulfonio, propildimetilsulfonio y similares; trialquilsulfoxonio, preferentemente en donde el número total de átomos de carbono en los tres sustituyentes alquilo no excede de más de seis aproximadamente, tales como trimetilsulfoxonio, etildimetilsulfoxonio, propildimetilsulfoxonio y similares; tetraalquilsulfonio, tales como tetrametilsulfonio, etiltrimetilsulfonio, propiltrimetilsulfonio y grupos similares,

[0058] En las composiciones deseables según esta invención, M se elige independientemente entre las mitades formadoras de sales agrícolamente aceptables anteriormente descritas e hidrógeno. En las composiciones más deseables, M es una mitad de metal alcalino, amonio, monoalquilamonio o trialquilsulfonio. En las composiciones especialmente deseables, solo una M es una mitad de metal alcalino, amonio, monoalquilamonio o trialquilsulfonio, mientras que las dos M son hidrógeno.

[0059] Composiciones particularmente deseables incluyen N-fosfonometilglicina de isopropilamina, N-fosfonometilglicina de trimetilsulfonio y sesqui-N-fosfonometilglicina sódica. Se pueden emplear combinaciones de dos o más compuestos PMCM en la formulación de la composición y métodos de la presente invención.

[0060] Los siguientes ejemplos son ilustrativos de la presente invención. Todas las cantidades se indican en peso salvo que se diga lo contrario.

[0061] Ejemplo 1

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad, en peso</u>
a	aceite mineral	44,12
b	solución de jarabe de maíz de alto contenido en fructosa	29,41
c	seboamina etoxilada	26,47

[0062] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

[0063] Ejemplo 2

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad, en peso</u>
a	aceite mineral	46,15
b	solución de jarabe de maíz de alto contenido en fructosa	15,38
c	seboamina etoxilada	30,77
d	alquil(C ₉ -C ₁₁)polisacárido	7,9

[0064] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

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[0065] Ejemplo 3

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad en peso</u>
a	aceite mineral	45,45
b	solución de jarabe de maíz de alto contenido en fructosa	18,16
c	seboamina etoxilada	30,30
e	dodecibencenosulfonato, sal de isopropilamina	6,06

[0066] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

[0067] Ejemplo 4

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad en peso</u>
a	aceite mineral	42,55
b	solución de jarabe de maíz de alto contenido en fructosa	25,55
c	seboamina etoxilada	28,37
f	monoolcato de sorbitan	3,55

[0068] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

[0069] Ejemplo 5

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad en peso</u>
a	aceite mineral	44,12
b	solución de jarabe de maíz de alto contenido en fructosa	14,71
c	seboamina etoxilada	29,41
d	alquil(C ₉ -C ₁₁)polisacárido	8,82
f	mono- y di-glicéridos	2,94

[0070] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

[0071] Ejemplo 6

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad en peso</u>
a	aceite mineral	43,17
b	solución de jarabe de maíz de alto contenido en fructosa	18,71
c	seboamina etoxilada	28,78
e	dodecilbencenosulfonato, sal de	7,19
f	isopropilamina	2,16
	monooleato de sorbitan	

[0072] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

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[0073] Ejemplo 7

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad, en peso</u>
a	aceite mineral	33,78
b	solución de jarabe de maíz de alto contenido en fructosa	14,93
c	seboamina etoxilada	29,85
d	alquil(C ₉ -C ₁₁)polisacárido	7,46
e	dodecilbencenosulfonato, sal de isopropilamina	2,99

[0074] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

[0075] Ejemplo 8

Se prepara el siguiente concentrado:

<u>Código componente</u>	<u>Nombre componente</u>	<u>Cantidad, en peso</u>
a	aceite mineral	37,97
b	solución de jarabe de maíz de alto contenido en fructosa	25,32
c	seboamina etoxilada	25,32
d	alquil(C ₉ -C ₁₁)polisacárido	6,33
e	dodecilbencenosulfonato, sal de	2,53
f	isopropilamina monooleato de sorbitan	2,53

[0076] El concentrado anterior se auto-emulsiona tras la dilución al 5% con agua. Cuando se incorporan 0,5 partes % (v/v) del compuesto agroquímico glifosato en el

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concentrado antes de la dilución en agua, la composición diluida es eficaz como un herbicida.

[0077] El experto en la materia podrá apreciar que la presente invención puede ponerse en práctica de forma distinta a las modalidades aquí descritas, las cuales se ofrecen solo con fines ilustrativos y de ningún modo limitativos.

REIVINDICACIONES

1. - Una composición homogénea y auto-emulsionante de un concentrado agroquímico a base de aceite que comprende:

- a al menos un componente de aceite;
- b al menos un sacárido no surfactante; y
- c alrededor de 0,5 a 50% en peso de al menos un surfactante,

en donde la relación en peso de dicho aceite a dichos sacárido no surfactante está comprendida entre 1:100 y 100:1 aproximadamente.

2. - Una composición homogénea según la reivindicación 1, en donde dicho al menos surfactante c. es no iónico.

3. - Una composición homogénea según la reivindicación 2, que comprende:

- a de 10 a 90 partes en peso aproximadamente de dicho al menos componente de aceite;
- b de 10 a 90 partes en peso aproximadamente de dicho al menos sacárido no surfactante, presente en solución; y
- c de 5 a 80 partes en peso aproximadamente de dicho al menos surfactante no iónico.

4. - Una composición homogénea según la reivindicación 1, que comprende:

- a de 10 a 90 partes en peso aproximadamente de al menos un componente de aceite;
- b de 10 a 90 partes en peso aproximadamente de al menos una solución de sacárido no surfactante; y
- c de 5 a 80 partes en peso aproximadamente de al menos un surfactante no iónico; y que además comprende al menos uno de los siguientes componentes adicionales:
- d de 1 a 20 partes en peso aproximadamente de al menos un hidrocarbilo sacárido surfactante; o

- e de 1 a 20 partes en peso aproximadamente de al menos un surfactante aniónico; o
- f de 1 a 20 partes en peso aproximadamente de al menos un surfactante no iónico adicional.

5. - Una composición según la reivindicación 4, en donde están presentes cada uno de los componentes d, e y f.

6. - Una composición según la reivindicación 4, en donde, en la composición del concentrado, las proporciones relativas en peso de los componentes son como sigue:

- a 25 a 75 aproximadamente,
- b 15 a 45 aproximadamente,
- c 5 a 60 aproximadamente,

y está presente al menos uno de los componentes d, e o f en una cantidad de:

- d 2 a 15 aproximadamente,
- e 2 a 15 aproximadamente,
- f 2 a 15 aproximadamente.

7. - Una composición según la reivindicación 6, en donde, en la composición del concentrado, las proporciones relativas en peso de los componentes son como sigue:

- a 30 a 60 aproximadamente,
- b 20 a 45 aproximadamente,
- c 10 a 45 aproximadamente,

y está presente al menos uno de los componentes d, e o f en una cantidad de:

- d 3 a 15 aproximadamente,
- e 3 a 15 aproximadamente,
- f 3 a 15 aproximadamente.

8. - Una composición según la reivindicación 2, en donde dicho componente de aceite a. de dicha composición del concentrado tiene un punto de ebullición por

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encima de 200° C.

9. - Una composición según la reivindicación 2, en donde dicho componente de aceite a. de dicha composición del concentrado comprende un aceite mineral, un aceite vegetal, un éster de un ácido graso C₁-C₂₂ o una mezcla de más de uno de los anteriores.

10. - Una composición según la reivindicación 2, en donde dicho sacárido no surfactante b. se elige del grupo consistente en un monosacárido, un oligosacárido y un polisacárido.

11. - Una composición según la reivindicación 2, en donde dicho surfactante no iónico c. tiene la fórmula:



en donde

R¹ es un grupo hidrocarbilo, hidrocarbonilo o hidrocarbamidilo, que adecuadamente contiene de 6 a 24, con preferencia de 8 a 22 y especialmente de 12 a 18 átomos de carbono, un grupo glicerol o poliglicerol o un grupo sorbitan o sorbitol;

A es una unidad de óxido de polialquileno que contiene una media de n grupos de óxido de alquileno o de grupos de óxido de alquileno mixtos, en donde los grupos alquileno tienen cada uno de 2 a 8, preferentemente 2 o 3, átomos de carbono;

n está comprendido entre 0 y 40, preferentemente entre 2 y 30 y más preferentemente entre 5 y 20;

R² es hidrógeno o un residuo hidrocarbonilo que tiene de 8 a 22 átomos de carbono, o un residuo de ácido policarboxílico que tiene de 2 a 6 átomos de carbono, tal como malato, fumarato, maleato, succinato o citrato, o un oligómero de los

mismos;

R³ es un grupo hidrocarbilo o hidrocarbonilo que tiene de 8 a 22 átomos de carbono, preferentemente de 12 a 18.

12. - Una composición según la reivindicación 9, en donde dicho componente de aceite a. está presente en una cantidad de 30 a 60 partes en peso aproximadamente y están presentes de 15 a 45 partes en peso aproximadamente de surfactante en total.

13. - Una composición según la reivindicación 11, en donde dicho surfactante no iónico c. se elige del grupo consistente en ácidos grasos alcoxilados, ésteres de polialquilenglicol, glicéridos alcoxilados, ésteres de sorbitan y de sorbitol alcoxilados, alcoxilatos de alquilfenol, alcoxilatos de alcoholes, alcoxilatos de alquilaminas, alcohol amidas y alcanolamidas alcoxiladas.

14. - Una composición según la reivindicación 4, en donde está presente al menos uno de dichos componentes d., e. o f. y dicho componente d. tiene la fórmula:



en donde

R es una mitad hidrófoba;

G es un residuo de sacárido; y

n tiene un valor medio de al menos 1;

y dicho componente e. tiene la fórmula:



en donde

R¹ es un grupo hidrocarbilo que tiene de 6 a 24 átomos de carbono, con preferencia de 8 a 22 átomos de carbono y más preferentemente de 12 a 18 átomos de carbono;

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- A** es una unidad de óxido de polialquileno que contiene una media de n grupos de óxido de alquileno o grupos de óxido de alquileno mixtos, en donde los grupos alquileno tienen cada uno de 2 a 8, con preferencia 2 o 3, átomos de carbono;
- n está comprendido entre 0 y 60, con preferencia entre 2 y 30 y más preferentemente entre 5 y 20;
- X** es un grupo que incluye al menos un átomo de H ácido o una sal del mismo;
- y dicho componente f tiene la fórmula:



en donde

- R¹** es un grupo hidrocarbilo, hidrocarbonilo o hidrocarbamidilo, que adecuadamente contiene de 6 a 24, con preferencia de 8 a 22 y especialmente de 12 a 18 átomos de carbono, un grupo glicerol o poliglicerol o un grupo sorbitan o sorbitol;
- A** es una unidad de óxido de polialquileno que contiene una media de n grupos de óxido de alquileno o de grupos de óxido de alquileno mixtos, en donde los grupos alquileno tienen cada uno de 2 a 8, preferentemente 2 o 3, átomos de carbono;
- n está comprendido entre 0 y 40, preferentemente entre 2 y 30 y más preferentemente entre 5 y 20;
- R²** es hidrógeno o un residuo hidrocarbonilo que tiene de 8 a 22 átomos de carbono, o un residuo de ácido policarboxílico que tiene de 2 a 6 átomos de carbono, tal como malato, fumarato, maleato, succinato o citrato, o un oligómero de los mismos;
- R³** es un grupo hidrocarbilo o hidrocarbonilo que tiene de 8 a 22 átomos de carbono, preferentemente de 12 a 18.

15. - Una composición según la reivindicación 14, en donde dicho componente d. está presente como un alquil poliglicósido de fórmula general:



en donde n es de 8 a 14 y b es mayor de o igual a 1 y menor de 3.

16. - Una composición según la reivindicación 14, en donde el componente e. se elige del grupo consistente en carboxilatos de alquilo y carboxilatos de alquiléter, sulfatos de alquilo y sulfatos de alquilo o de alquilfeniléter, fosfatos de alquilo o de alquilfenilo y fosfatos de alquilo o de alquilfeniléter, sulfosuccinatos de alquilo o de alquilfenilo y sulfosuccinatos de alquilo o de alquilfeniléter, sulfonatos de alquilo o de alquilfenilo y fosfonatos de alquilo o de alquilfenilo.

17. - Una composición según la reivindicación 14, en donde el componente f. se elige del grupo consistente en ésteres de glicerol o de poliglicerol, ésteres de sorbitol o de sorbitan, ésteres de etilen- o de propilenglicol, ésteres de polietilenglicol o alcoholes grasos.

18. - Método de uso de la composición según la reivindicación 2, en donde dicho concentrado se emulsiona tras la dilución en agua y la formulación diluida comprende además un compuesto agroquímico.

19. - Método de uso de la composición según la reivindicación 2, en donde dicho concentrado se emulsiona tras la dilución en agua y el compuesto agroquímico es un herbicida, bien selectivo o bien no selectivo.

20. - Método de uso de la composición según la reivindicación 2, en donde dicho concentrado se emulsiona tras la dilución en agua y el compuesto agroquímico consiste en uno o más compuestos reguladores del crecimiento, herbicidas y/o pesticidas.

21. - Método según la reivindicación 18, en donde la cantidad de agua usada

para diluir el concentrado es de 10 a 10.000 veces el peso de la composición del concentrado.

22. - Método para el tratamiento de vegetación mediante aplicación a las plantas y/o al suelo de una formulación diluida preparada en la forma reivindicada en la reivindicación 19.

23. - Método según la reivindicación 19, en donde el compuesto agroquímico consiste en al menos un herbicida de fosfonometil-N-carboximetilo de fórmula:



en donde:

cada R^1 es independientemente halógeno, $-NHOH$, $-N(R^2)_2$, $-OR^3$, SR^3 o $-OM$,

en donde R^2 es independientemente hidrógeno o alquilo o hidroxialquilo, alquenilo, o fenilo;

cada R^3 es independientemente hidrógeno, alquilo, hidroxialquilo o cloroalquilo, alcoxi, alquilenamina, fenilo o bencilo;

M es hidrógeno o representa mitades formadoras de sales agrícolamente aceptables, tales como mitades de metales alcalinos, metales alcalinotérreos, estánnicas, amónicas, amónicas orgánicas, alquilsulfonio, alquilsulfoxonio, alquifosfonio o combinaciones de las anteriores; y

Z es hidrógeno, una mitad orgánica o una mitad inorgánica.

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RESUMEN

Concentrados emulsionables a base de aceite que contienen un sacárido líquido y que incluyen a) al menos un componente de aceite; b) al menos un sacárido, en particular una solución de sacárido líquido (LS); c) y al menos un surfactante no iónico. El concentrado puede contener también al menos uno de d) al menos un hidrocarbilo sacárido surfactante; o e) al menos un surfactante aniónico; o f) al menos otro surfactante no iónico soluble en aceite. Los concentrados son normalmente homogéneos durante al menos 24 horas y se emulsionan fácilmente tras la dilución en agua. Los concentrados pueden contener también un agente antiespumante, especialmente un polisiloxano. Tras la dilución en agua, las emulsiones formadas a partir de los concentrados se aplican a sustratos en combinación con ingredientes agroquímicamente activos, con preferencia N-fosfonometilglicina en forma de sus sales solubles, para controlar malas hierbas.

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

MAYER BROWN ROWE & MAW LLP
Intellectual Property Group
Attn. Sharer, Paul L.
1909 K Street, N.W.
Washington D.C. WA 20006-1101
UNITED STATES OF AMERICA

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

Status - UPS

AMND2

(PCT Rule 44.1)

Applicant's or agent's file reference

04280908

Date of mailing
(day/month/year)

12/11/2004

Search
Recd Date

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/US2004/014401 ✓

International filing date
(day/month/year)

07/05/2004

Applicant

ICI AMERICAS, INC.

1. ☒ 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 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ 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.

3. ☐ 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.

4. 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.3, 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 20 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/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.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
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Authorized officer

Angela Lopez Navarro

These Notes are intended to give the basic instructions concerning the filing of amendments under article 18. 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 18

The applicant has, after having received the international search report, 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 18 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.

What parts of the international application may be amended?

Under Article 18, 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 48.1).

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 48.2).

Where a demand for international preliminary examination has been/is 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.

7/10/94

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 46 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 46 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Office, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 04280908	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/US2004/014401	International filing date (day/month/year) 07/05/2004	(Earliest) Priority Date (day/month/year) 07/05/2003
Applicant ICI AMERICAS, INC.		

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 4 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 III).

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:

HOMOGENEOUS LIQUID COMPOSITIONS COMPRISING SACCHARIDE AND OIL

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regards 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.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/014401

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N25/02 A01N43/08 A01N57/20 A01N57/04 A01N57/06
A01N57/26
/(A01N43/08,A01N57:20),(A01N43/08,A01N57:04),(A01N43/08,A01N57:06)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 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, PAJ, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 945 377 A (PENNER DONALD ET AL) 31 August 1999 (1999-08-31) cited in the application	1,2, 8-10, 18-23
Y	column 3, lines 7-9 - lines 25-67; claim 4; example 14; table 11	3-7, 11-17
X	DAHL G K ET AL DAHL G K ET AL: "Adjuvant and adjuvant components influence on performance of various herbicides. Adjuvant and adjuvant components influence on performance of various herbicides." PROC.NORTH CENT.WEED SCI.SOC., vol. 56, 2001, page 138, XP001203640	1,2, 8-10, 18-23
Y	abstract	3-7, 11-17
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in 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 doubt on priority claim(s) or which is cited to establish the publication date of another claim or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

8 November 2004

Date of mailing of the international search report

12/11/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentplan 2
NL - 2200 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 apo nl,
Fax: (+31-70) 340-3016

Authorized officer

Romano-Götsch, R

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US2004/014401

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 79/00838 A (SAMPSON MICHAEL JAMES) 18 October 1979 (1979-10-18) page 2, line 7 - line 11 page 7 page 12; example IX page 20; example 10	1-3, 8-13, 18-22
Y	US 2 447 475 A (KABERG RUSSELL A ET AL) 17 August 1948 (1948-08-17) column 1, line 13 - line 23; claim 5; example IV	1-23
Y	WO 95/03881 A (HOORNE DIRK ; ALDA MAHROUSSA (BE); ROGIERS LODEWIJK MARIA (BE); ICI PL) 9 February 1995 (1995-02-09) cited in the application page 1, line 1 - line 16 page 1, paragraph 25 - page 2, paragraph 19 page 6, line 8 - line 29 page 11; example 1	1-23
A	DE 100 64 406 A (COGNIS DEUTSCHLAND GMBH) 27 June 2002 (2002-06-27) page 2, lines 15-19, paragraph 4 page 3, paragraph 9 page 4, paragraphs 15,17 page 5, paragraph 20; claims 12,13	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/014401

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5945377	A	31-08-1999	CA 2304563 A1	10-06-1999
			WO 9927787 A1	10-06-1999
WO 7900838	A	18-10-1979	CA 1148761 A1	28-06-1983
			DE 2943229 T0	11-12-1980
			DK 502779 A	27-11-1979
			EP 0020337 A1	07-01-1981
			FR 2475851 A1	21-08-1981
			WO 7900838 A1	18-10-1979
			GB 2030452 A ,B	10-04-1980
			JP 55500166 T	27-03-1980
			NL 7902380 A	02-10-1979
			SE 447326 B	10-11-1986
			SE 8003121 A	24-04-1980
			US 4436547 A	13-03-1984
			ES 478971 A1	01-08-1979
US 2447475	A	17-08-1948	NONE	
WO 9503881	A	09-02-1995	AT 216911 T	15-05-2002
			AU 695243 B2	13-08-1998
			AU 7233594 A	28-02-1995
			CA 2168015 A1	09-02-1995
			DE 69430533 D1	06-06-2002
			DE 69430533 T2	31-10-2002
			DK 707514 T3	19-08-2002
			EP 0707514 A1	24-04-1996
			ES 2176249 T3	01-12-2002
			WO 9503881 A1	09-02-1995
			JP 9500825 T	28-01-1997
			NZ 268936 A	26-01-1998
			PT 707514 T	30-09-2002
			US 6586366 B1	01-07-2003
			ZA 9405520 A	30-03-1995
DE 10064406	A	27-06-2002	DE 10064406 A1	27-06-2002

PATENT COOPERATION TREATY

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From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

see form PCT/ISA/220

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.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/US2004/014401

International filing date (day/month/year)
07.05.2004

Priority date (day/month/year)
07.05.2003

International Patent Classification (IPC) or both national classification and IPC
A01N25/02, A01N43/08, A01N57/20, A01N57/04, A01N57/06, A01N57/26

Applicant
ICI AMERICAS, INC.

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 43bis.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 66.1bis(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-80298 Munich
Tel. +49 89 2369 - 0 Tx: 523656 apmu d
Fax: +49 89 2369 - 4465

Authorized Officer

Romano-Götach, R

Telephone No. +49 89 2369-8874



**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/US2004/014401

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:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No. **PCT/US2004/014401**

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

1. Statement

Novelty (N)	Yes: Claims	4-7, 14-17
	No: Claims	1-3, 8-13, 18-23
Inventive step (IS)	Yes: Claims	
	No: Claims	1-23
Industrial applicability (IA)	Yes: Claims	1-23
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V.

1. The following documents are referred to in this communication:

D1 : US-A-5 945 377 (1999-08-31)

D2 : DATABASE CROPU [Online] 2003, DAHL ET AL: "Adjuvant and adjuvant components influence on performance of various herbicides. Adjuvant and adjuvant components influence on performance of various herbicides." XP002303866 retrieved from STN Database accession no. 2003-85865

D3: WO-A-79/00838 (1979-10-18)

D4 : US-A-2 447 475 (1948-08-17)

D5: WO-A-95/03881(1995-02-05)

2. INDEPENDENT CLAIM 1

Novelty

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 1 is not new in the sense of Article 33(2) PCT.

Document D1 discloses agrochemical compositions comprising a monosaccharide (column 3, lines 24-32), surfactants and vegetable oils (column 3, lines 41-55).

In Table 11, column 11, composition nr 14, a spray mixture comprising Round-up Ultra (Glyphosate + surfactants e.g. phosphate esters and cationic tallow amines); Scoll (methylated rape-seed oil) and Isoclear 55 (fructose corn syrup) is disclosed. According to D1, the compositions are preferably in the form of concentrates, diluted prior use in the fields (column 3, lines 7-24).

Document D2 describes compositions containing a herbicide and a modified concentrated oil crop (COC) containing an emulsifier, paraffinic oil and fructose corn syrup. In an example, the crop was treated with a composition comprising glyphosate, emulsifiers and fructose corn syrup.

Document D3 describes an agricultural composition comprising a pesticide and at least one additive selected from (a) to (h) according to pp.2-3. On p.20 Example 10 and p.12 (example IX), compositions comprising a pesticide and the additives olive oil, alkyl phenol ethylene oxide and sucrose are described. According to p.2, lines 9-11, the formulations may be in the form of concentrate, subsequently diluted with water to make them ready for use.

D4-D5 are not relevant to the novelty of the claimed matter on file.

Inventive Step

The present application does not meet the criteria of Article 33(1) PCT, because the

subject matter of claim 1 does not involve an inventive step in the sense of Article 33(3)PCT.

The subject-matter of claim 1 is already known from D1-D3. Therefore, an inventive step over D1-D3 cannot be acknowledged.

The claimed matter 1 is not regarded as inventive over D4 combined with D1 or D2 (Article 33(3) PCT).

The problem to be solved by the application is regarded as the provision of an alternative homogeneous self-emulsifying oil-based agrochemical concentrate.

The solution proposed in the application is the provision of a concentrate comprising at least one oil component, at least one non-surfactant saccharide, about 0.5% to about 50% by weight of at least one surfactant, wherein the weight ratio of said oil to said saccharide is between about 1:100 and about 100:1.

D4, which deals with the same technical problem as the application (see column 1, lines 13-22), discloses compositions comprising an oil soluble pesticide, an oil, a nonionic surfactant and an anionic surfactant. A saccharide is not present.

D1 teaches that saccharides, e.g. corn syrup, enhance the activity of herbicides, e.g. glyphosate and glufosinate (see column 8, lines 28-67), and can be combined with several adjuvants, including oil and surfactants (see example 14 in Table 11).

D2 teaches combining glyphosate with a COC modified with corn syrup.

In view of the teaching of D1 or D2, it appears obvious to add a saccharide to the compositions disclosed in D4 and, thus, to achieve the compositions on file.

Therefore the features disclosed in D4 and D1 or D2 would be combined by the skilled person, without exercise of any inventive skills in order to solve the problem posed.

The claimed matter 1 is not regarded as inventive over D5 combined with D1 or D2 (Article 33(3) PCT).

D5 discloses a readily emulsifiable surfactant composition comprising a pesticide, at least one oil, at least one surfactant saccharide and at least one nonionic surfactant (see p.1, lines 1-21, and p. 6, line 13, embodiment (i)). In view of the teaching of D1 and D2, it appears obvious to prepare a concentrate further comprising a saccharide.

3 DEPENDENT CLAIMS 2-23

Dependent claims 1-3, 8-13, 18-23 do not contain any features which, in combination with the features of any claim to which they refer, render them novel or inventive over D1, D2 and D3.

Claims 4-7, 14-17 meet the requirements of the PCT in respect of novelty (Art. 33(2)PCT), but are not regarded as inventive in view of D5 (pp.2-4) in combination with D1 or D2.

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) 04280908

Box No. I TITLE OF INVENTION	
HOMOGENEOUS LIQUID SACCHARIDE AND OIL SYSTEMS	
Box No. II APPLICANT ☐ This person is also inventor	
Name and address: (Family name followed by given names; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)	
ICI AMERICAS, INC. 10 Findeme Avenue Bridgewater, New Jersey 08807 United States of America	
Telephone No.	
Facsimile No.	
Teleprinter No.	
Applicant's registration No. with the Office	
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given names; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)	
LINDNER, Greg J. 18 Hayloft Circle Wilmington, Delaware 19808 United States of America	
This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (if this check-box is marked, do not fill in below.)	
Applicant's registration No. with the Office	
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative	
Name and address: (Family name followed by given names; for a legal entity, full official designation. The address must include postal code and name of country.)	
SHARER, Paul L. Intellectual Property Group Mayer Brown Rowe & Maw LLP 1909 K Street, N.W. Washington, D.C. 20006-1101	
Telephone No. (202) 263-3340	
Facsimile No. (202) 263-3300	
Teleprinter No.	
Agent's registration No. with the Office 36,004	
☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

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Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.

However,

- ☐ DE Germany is not designated for any kind of national protection
- ☐ KR Republic of Korea is not designated for any kind of national protection
- ☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may be used to exclude (irrevocably) the designations concerned in order to avoid the causing of the effect, under the national law, of an earlier national application from which priority is claimed. See the Notes to Box No. V as to the consequences of such national law provisions in these and certain other States.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1) 07 May 2003 (07.05.03)	10/431,616	US		
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☒ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EPO

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of declarations

- ☐ Box No. VIII (i) Declaration as to the identity of the inventor :
- ☐ Box No. VIII (ii) Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent :
- ☐ Box No. VIII (iii) Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application :
- ☐ Box No. VIII (iv) Declaration of inventorship (only for the purposes of the designation of the United States of America) :
- ☐ Box No. VIII (v) Declaration as to non-prejudicial disclosures or exceptions to lack of novelty :

Box No. IX CHECK LIST; LANGUAGE OF FILING																																																								
This international application contains: (a) in paper form, the following number of sheets: <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 80%;">request (including declaration sheets) :</td> <td style="width: 20%; text-align: right;">3</td> </tr> <tr> <td>description (excluding sequence listing and/or tables related thereto) :</td> <td style="text-align: right;">20</td> </tr> <tr> <td>claims :</td> <td style="text-align: right;">6</td> </tr> <tr> <td>abstract :</td> <td style="text-align: right;">1</td> </tr> <tr> <td>drawings :</td> <td style="text-align: right;">0</td> </tr> <tr> <td>Sub-total number of sheets :</td> <td style="text-align: right; border-top: 1px solid black;">30</td> </tr> <tr> <td>sequence listing :</td> <td style="text-align: right;">0</td> </tr> <tr> <td>tables related thereto :</td> <td style="text-align: right;">0</td> </tr> <tr> <td colspan="2" style="padding-top: 5px;"> <i>(for both, actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (c) below)</i> </td> </tr> <tr> <td>Total number of sheets :</td> <td style="text-align: right; border-top: 1px solid black;">30</td> </tr> </table> (b) ☐ only in computer readable form (Section 801(a)(i)) (i) ☐ sequence listing (ii) ☐ tables related thereto (c) ☐ also in computer readable form (Section 801(a)(ii)) (i) ☐ sequence listing (ii) ☐ tables related thereto Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the ☐ sequence listing: ☐ tables related thereto: <i>(additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)</i>	request (including declaration sheets) :	3	description (excluding sequence listing and/or tables related thereto) :	20	claims :	6	abstract :	1	drawings :	0	Sub-total number of sheets :	30	sequence listing :	0	tables related thereto :	0	<i>(for both, actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (c) below)</i>		Total number of sheets :	30	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item): <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 80%;">1. ☒ fee calculation sheet</td> <td style="width: 20%; text-align: right;">1</td> </tr> <tr> <td>2. ☐ original separate power of attorney</td> <td style="text-align: right;">:</td> </tr> <tr> <td>3. ☐ original general power of attorney</td> <td style="text-align: right;">:</td> </tr> <tr> <td>4. ☐ copy of general power of attorney; reference number, if any:</td> <td style="text-align: right;">:</td> </tr> <tr> <td>5. ☐ statement explaining lack of signature</td> <td style="text-align: right;">:</td> </tr> <tr> <td>6. ☐ priority document(s) identified in Box No. VI as item(s):</td> <td style="text-align: right;">:</td> </tr> <tr> <td>7. ☐ translation of international application into (language):</td> <td style="text-align: right;">:</td> </tr> <tr> <td>8. ☐ separate indications concerning deposited microorganism or other biological material</td> <td style="text-align: right;">:</td> </tr> <tr> <td>9. ☐ sequence listing in computer readable form (indicate type and number of carriers)</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="margin-left: 20px;">(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) :</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="margin-left: 20px;">(ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter :</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="margin-left: 20px;">(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column :</td> <td style="text-align: right;">:</td> </tr> <tr> <td>10. ☐ tables in computer readable form related to sequence listing (indicate type and number of carriers)</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="margin-left: 20px;">(i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application) :</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="margin-left: 20px;">(ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quater) :</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="margin-left: 20px;">(iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column :</td> <td style="text-align: right;">:</td> </tr> <tr> <td>11. ☐ other (specify):</td> <td style="text-align: right;">:</td> </tr> </table>	1. ☒ fee calculation sheet	1	2. ☐ original separate power of attorney	:	3. ☐ original general power of attorney	:	4. ☐ copy of general power of attorney; 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Figure of the drawings which should accompany the abstract: n/a	Language of filing of the international application: English																																																							

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Paul L. Sharer (Reg. 38,004)	Date: May 7, 2004
-------------------------------------	--------------------------

For receiving Office use only	
1. Date of actual receipt of the purported international application:	2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

PCT

FEE CALCULATION SHEET Annex to the Request

For receiving Office use only

International Application No.

Date stamp of the receiving Office

Applicant's or agent's
file reference

04280908

Applicant

ICI AMERICAS, INC. et al.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE USD 300 T

2. SEARCH FEE 1,920 S

International search to be carried out by EPO
(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FILING FEE

Where items (b) and/or (c) of Box No. IX apply, enter Sub-total number of sheets } 30
Where items (b) and (c) of Box No. IX do not apply, enter Total number of sheets }

i1 first 30 sheets 1,134 i1

i2 0 x 12 = 0 i2
number of sheets in excess of 30 fee per sheet

i3 additional component (only if sequence listing and/or tables related thereto are filed in computer readable form under Section 801(a)(i), or both in that form and on paper, under Section 801(a)(ii)):

400 x = 0 i3
fee per sheet

Add amounts entered at i1, i2 and i3 and enter total at I 1,134 I

(Applicants from certain States are entitled to a reduction of 75% of the international filing fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the international filing fee.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) 20 P

5. TOTAL FEES PAYABLE USD 3,374
Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

MODE OF PAYMENT

- ☒ authorization to charge deposit account (see below) ☐ postal money order ☐ cash ☐ coupons
☐ cheque ☐ bank draft ☐ revenue stamps ☐ other (specify):

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all receiving Offices)

- ☒ Authorization to charge the total fees indicated above.
☒ (This check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.
☒ Authorization to charge the fee for priority document.

Receiving Office: RO/ US
Deposit Account No.: 503-121
Date: May 7, 2004
Name: Paul L. Sharer (36,004)
Signature: Paul L. Sharer

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

BRUESS, Steven C.
Merchant & Gould, P.C.
P.O. Box 2803
Minneapolis, MN 55402-0803
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 19 October 2004 (19.10.2004)	
Applicant's or agent's file reference 80137.2WOU1 ✓	IMPORTANT NOTIFICATION
International application No. PCT/US04/012472 ✓	International filing date (day/month/year) 21 April 2004 (21.04.2004) ✓
International publication date (day/month/year)	Priority date (day/month/year) 30 May 2003 (30.05.2003)
Applicant PHARMASSET, LTD. et al ✓	

1. By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. (If applicable) The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
3. (If applicable) An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
30 May 2003 (30.05.2003) ✓	80/474,388 ✓	USA ✓	10 September 2004 (10.09.2004)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Zoltanski Andrzej

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27
18

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION	()	☒
MODELO DE UTILIDAD	()	☒
- Indicación de que se solicita la concesión de una patente.	()	☒
- Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	☒
- Descripción de la invención.	()	☒
- Dibujos de ser estos pertinentes.	()	☒
- Comprobante de Pago de las tasas establecidas.	()	☒

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 o 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 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 de trazado	()	()
- Comprobante de pago de las tasas establecidas.	()	()

COMPLETA ()

INCOMPLETA () ()

Firma Responsable:



Fecha:

SUPERINDUSTRIA Y COMERCIO

Radicación : 95122645 00000000

Folios: 76

Fecha (AMD): 2015-12-02 16:25:46

Trámite : 011 PCT-PATENT 379 PAGE 0001 ALL PRESENTING
Dependencia: 2000 DIVISION DE NUEVAS CREACIONES

28
19

REPUBLICA DE COLOMBIA
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Bogotá,
2020

Doctor(a)
RODRIGUEZ D'ALEMAN DILIA MARIA
Apoderado(a) y/o Representante de
ICI AMERICAS INC.

REFERENCIA	Radicación No.	5 122665
	Solicitud internacional	US2004/014401
	Fecha inicio fase nacional	07/12/2005
	Trámite	11
	Evento	379
	Actuación	430
	Oficio No.	779

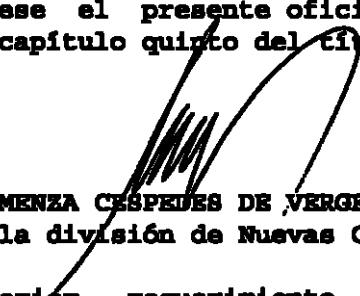
Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se 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. El solicitante deberá aclarar el nombre del inventor por cuanto difiere el presentado en la publicación internacional, con el aportado en el petitorio 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 Única No.10 de 2001.


ALIX CARMONA CRESPO DE VERGEL
Jefe de la división de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista de
fecha 27 Ene 2006
adpall