

**FORMULARIO UNICO DE CORRECCIONES Y MODIFICACIONES
2000-10**

1

SOLICITUD DE:



Corrección de Error Material



Modificación a una solicitud

2

SOLICITANTE

Nombre: **MONSANTO
TECHNOLOGY LLC**

sociedad constituida y existente bajo las leyes
del Estado de Delaware, Estados Unidos de
América

Dirección: 800 North Lindbergh
Boulevard, St. Louis,
Missouri 63167,
Estados Unidos de América

Teléfono: 546 09 70

E-mail: clientes@camyp.com

Fax: 249 40 70

Domicilio: St. Louis, Missouri, Estados
Unidos de América

IDENTIFICACION

C.C.



NIT



C.E.



Otro



Número: _____

3

**REPRESENTANTE
O APODERADO**

Nombre: Emilio FERRERO

Dirección: Carrera 4ª No. 72-35

Teléfono: 347 36 11

E-mail: cavelier@cavelier.com

Fax: 217 92 11

Domicilio: Bogotá, Colombia

IDENTIFICACION

C.C.



NIT



C.E.



Otro



Número: 438.019 TP 31.929

4

Número de expediente: 00.029.094

Título del Invento: **MÉTODO PARA MEJORAR LA EFECTIVIDAD BIOLÓGICA DE
COMPOSICIONES PARA EL TRATAMIENTO DE PLANTAS CONTENIENDO
GLIFOSATO U OTRAS SUSTANCIAS QUÍMICAS EXOGENAS ANIÓNICAS**

5

Descripción de la corrección o modificación solicitada:

Atentamente pido a usted se sirva ordenar la anotación en los libros de la Propiedad Industrial el cambio de nombre de la sociedad **MONSANTO COMPANY** por el de **PHARMACIA CORPORATION** domiciliada en 800 North Lindbergh Boulevard, St. Louis, Missouri 63167, Estados Unidos de América. Esta sociedad a la vez traspasó el derecho a la patente que se tramita en este expediente a **MONSANTO TECHNOLOGY LLC** domiciliada en 800 North Lindbergh Boulevard, St. Louis, Missouri 63167, Estados Unidos de América.

Por lo tanto, le solicito se sirva expedir el certificado de patente a favor de la sociedad **MONSANTO TECHNOLOGY LLC**.

6

Comprobante de pago No. 03-72,732 Fecha: 7 de octubre de 2003

Comprobante de pago No. 03-75,097 Fecha: 15 de octubre de 2003

7

Anexos:



Comprobantes de pago de la tasa por \$ 82.000.00 c/u.

322
315



Poderes, si fuere el caso



Certificado de existencia y representación legal, cuando el solicitante sea persona jurídica



Documentos que acreditan el cambio de nombre y el traspaso.



NOMBRE: EMILIO FERRERO

FIRMA: *Emilio Ferrero*
C.C. 438.019 de Usaquén T.P. 31.929

266

JGG-65

12946
6324 14
316

322

Apostille

(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

This public document

2. has been signed by JUDITH A. LORENZ

3. acting in the capacity of NOTARY PUBLIC

4. bears the seal/stamp of JUDITH A. LORENZ-NOTARY PUBLIC-STATE OF MISSOURI

Certified

5. at Jefferson City, Missouri

6. the 29th day of MAY, 2001

7. by Matt Blunt, Secretary of State, State of Missouri

8. No. 63157

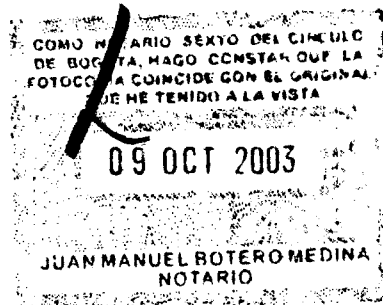
9. Seal/Stamp

10. Signature:

Matt Blunt

Comm. 48 (12-2000)

TRADUCCION No. 1506/01
MARIA ELVIRA MARTÍLO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia



CAVELIER

ABOGADOS

EDIFICIO SISKI
CARRERA 4a N° 72-35
BOGOTA, 8 - COLOMBIA

181

Representación y Poder con autenticación notarial y Apostille para patentes, modelos de utilidad, diseños industriales, marcas de fábrica, nombres comerciales, enseñas, nombres de dominio, lemas comerciales, licencias.

Representation and Power-of-Attorney with notarial authentication and Apostille for patents, utility models, industrial designs, trademarks, commercial names, trade emblems, domain names, slogans, licenses.

REPRESENTACION Y PODER

REPRESENTATION AND POWER-OF-ATTORNEY

Yo (nosotros), abajo firmado (s)/I (we), the undersigned
MONSANTO TECHNOLOGY LLC

domiciliado (s) en/or 800 North Lindbergh
Boulevard, St. Louis, Missouri 63167,
United States of America,

por el presente nombramos a EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PAEZ, tpa. 23555 y GERMAN CAVELIER, tpa. 832, domiciliados en la Carrera 4a N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el párrafo 1o del Artículo 543 del Código de Comercio, el primero como principal y los demás como suplentes, en su orden, como mis (nuestros) representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquél. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o el tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambos, declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario u otro Funcionario Público, o Cónsul de Colombia, en el extranjero; y si se tratare de impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cesare la ausencia o impedimento del representante principal, o de su primero o segundo suplentes, en su caso, podrán ejercer la representación, en su orden, uno u otros según el caso, asumiéndola por el solo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero, segundo o tercer suplente en su caso.

Además, confiero (conferimos) poder a los abogados arriba nombrados, para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal, a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas, ejerzan o no jurisdicción, especialmente ante las del orden administrativo, contencioso-administrativo y judicial, así como los tribunales de arbitramento, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes de invención, modelos de utilidad y diseños industriales; el registro de marcas de fábrica, colectivas, defensivas, de servicio, lemas comerciales, nombres comerciales, enseñas, nombres de dominio, variedades vegetales y denominaciones de origen; su renovación, traspaso, cambio de nombre o domicilio, cancelación voluntaria; y el registro de licencias de uso de esos derechos; b) Las acciones de competencia desleal, protección del consumidor, oposiciones u observaciones, cancelación administrativa y judicial, nulidad, medidas cautelares, concesión de licencias, la tutela, la protección de secretos industriales, y en general los juicios civiles, penales, administrativos o contencioso-administrativos relacionados con

in due compliance with the terms of paragraph 1st. of article 543 of the Commercial Code, do hereby appoint EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PAEZ, tpa. 23555 and GERMAN CAVELIER, tpa. 832, domiciled at Carrera 4a N° 72 35, Bogotá, Colombia, the first as principal and the others as alternates, in the order of their appointment, as our representatives for all industrial property matters with faculty to receive notifications and to appoint attorneys in and out of Court. The first alternate shall replace the principal in case of his absence or of temporal or definitive impediment. The same rule will apply when the second alternate representative is to replace the first one, or when the third is to replace the first or second alternates in their turn, or both of them, second. In such cases, the principal representative, or the first or second alternates in their turn, or both of them, shall state their intention not to act as representatives through a declaration given before a Notary Public in Colombia, or before a Notary or another Public Official or a Colombian Consul abroad; and in case of impediment, the appropriate certificate shall suffice. If any of the appointees were to be definitely absent, the following alternate shall take his place. When the absence or impediment of the principal representative, or of the first or second alternate in their turn ceases, the representation can be taken again in their sequence, by the principal, the first or second alternate depending on case, and the mere fact or its exercise will suffice. The exercise of the representation by the first, second or third alternates in their turn shall end at such time. In addition, we grant a Power of Attorney to the above named attorneys at law so that they may obtain and defend my (our) industrial property and against the unfair competition; for which purpose I (we) authorize the said attorneys to represent me (us) before any authorities or persons, with or without jurisdiction, specially those administrative, administrative contentious and judicial, as well as before Arbitration Court, in all matters concerning the following: a) Obtainment of patents, utility models and industrial designs; the registration of trademarks, collective, defensive and service marks, slogans, commercial names, trade emblems, domain names, vegetal varieties and denominations of origin; its renewal, assignment, change of name or domicile, voluntary cancellation; and the registration of licenses of use of the above rights; b) Actions of unfair competition, protection to the consumer, oppositions or observations, administrative or Court cancellation, nullity, infringement, granting of licenses, the action for writ mandamus, the protection of trade secrets, and in general the civil, penal, and administrative suits relating to those rights; actions and suits

TRADUCCION No.: 15.06101
MARIA ELVIRA MARTELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2079 Min. Justicia

estos derechos; acciones y procesos que promovamos o se nos promuevan. Y para que en todos los asuntos arriba determinados, puedan sustituir este mandato, transigir, conciliar, admitir los hechos del proceso, desistir, cancelar, recibir, renunciar, y ratificar los actos de agentes oficiosos.

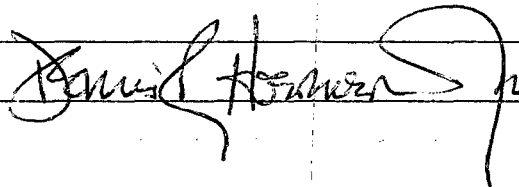
instituted by me (us) or against me (us). And that in all the above matters they may substitute this Power of Attorney, compromise, conciliate, admit the facts of the case, desist, cancel, receive, resign, and ratify acts done by representatives without a power of attorney.

Dado y firmado hoy/Given and signed this 21st day of May, 2001

en/in St. Louis, MO

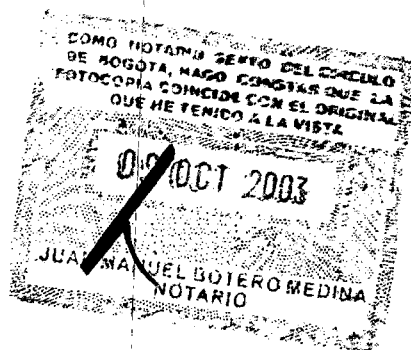
por/by Dennis R. Hoerner, Jr. ✓

Firma



Signature

TRADUCCION No.: 15.06/01
MARIA ELVIRA MARTELLO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia



CERTIFICADO NOTARIAL (INDIVIDUO)

A los _____ días del mes de _____
de 200__ ante mí, Notario Público o Funcionario Autorizado
de _____
compareció(eron) personalmente _____

a quien(es) doy fe de conocer y me consta que es(son) la(s)
persona(s) firmante(s) del documento que precede, y quien(es)
tiene(n) capacidad legal para otorgarlo

Notario Público o Funcionario Autorizado --Notary Public or Attesting Official

CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy 18 de Mayo de 2001
Compareció(eron) ante mí

Dennis R. Hoerner, Jr.
quien(es) conozco personalmente y que firma(n) este
documento en representación de la Sociedad/compañía
denominada

MONSANTO TECHNOLOGY LLC

ertifico:

1. Que he visto los siguientes documentos:*

Acción de Miembro Unico, firmado en
Saint Louis, Missouri el 15/03/2001

2. Que dichos documentos prueban lo siguiente:

2.1. Que MONSANTO TECHNOLOGY LLC

es una Sociedad/Compañía legalmente constituida y existente
de acuerdo con las leyes de Estado de Delaware,
Estados Unidos de América.

2.2. Que el domicilio de dicha Sociedad/Compañía es _____
800 North Lindbergh Boulevard,
St. Louis, Missouri 63167, Estados
Unidos de América.

2.3. Que el objeto u objetos para los cuales se otorga el presente
poder están comprendidos dentro del objeto social de la
mencionada Sociedad/Compañía.

2.4. Que el(los) Sr.(Sres.) Dennis R. Hoerner Jr,
Presidente.
está(n) autorizado(s) para otorgar el presente Poder.

Ciudad St. Louis

Estado Missouri/USA

Hoy 18 de Mayo de 2001

Notario Público o Funcionario Autorizado -- Notary Public or Attesting Official

Los documentos deben identificarse con fecha y origen

NOTARIAL CERTIFICATE (INDIVIDUAL)

305
318

On this _____ day of _____
200__ before me, a Notary Public or Attesting Official of _____
personally appeared _____

to me known, and known to me to be the person(s) who
executed that foregoing document, and who has(have) legal
capacity to execute it.

NOTARIAL CERTIFICATE (CORPORATION)

On this 18th day of May 2001
appeared before me

Dennis R. Hoerner, Jr.
who(m) I know personally and who(m) signed this document as
representative(s) of the Corporation/Company named

MONSANTO TECHNOLOGY LLC

I certify:

1. That I have seen the following documents:*

ACTION OF SOLE MEMBER, SIGNED IN
ST. LOUIS? MISSOURI ON MARCH 15, 2001

2. That the above documents duly prove the following:

2.1. That MONSANTO TECHNOLOGY LLC

is a Corporation/Company legally constituted and in existence
in accordance with the laws of the State of Delaware,
United States of America,

2.2. That the domicile of said Corporation/Company is _____
800 North Lindbergh Boulevard,
St. Louis, Missouri 63167, United
States of America.

2.3. That the purpose or purposes for which the present Power
of Attorney is granted are corporate purposes of the
purposes set forth in the charter of the mentioned
Corporation/Company.

2.4. That Mr.(Messrs.) Dennis R. Hoerner, Jr,
President
is(are) authorized to grant the present Power of Attorney.

City St. Louis

State Missouri US

This 18th day of May 2001

JUDITH A. LORENZ
Notary Public - State of Missouri
St. Louis County
My Commission Expires: November 20, 2003

* Documents must be identified with date and origin

Excmo. Sr. Notario
C-10741-80-00-3
5

APOSTILLE (Convention de La Haye du 5 octobre 1961)	
1. Country:	
This public document	
2. has been signed by	
3. acting in the capacity of	
4. bears the seal/stamp of	
Certified	
5. at	6. the
7. by	
8. No.	
9. Seal/stamp	10. Signature
.....	

COMO NOTARIO SEXTO DEL CIRCULO
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA

19 OCT 2003

JUAN MANUEL ANTEPOMEDINA
NOTARIO

336 319

TRADUCCIÓN OFICIAL No. 15.06/01 preparada por María Elvira Martelo, traductora oficial aprobada por el Ministerio de Justicia mediante Resolución No. 2879 de 1995 y reconocida por el Ministerio de Relaciones Exteriores.

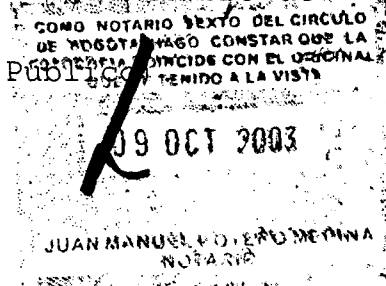
(A continuación se traducen los sellos y legalizaciones de un documento de Representación, Ratificación y Poder escrito en inglés y español, por el cual **MONSANTO TECHNOLOGY LLC**, domiciliada en 800 North Lindbergh Boulevard, St. Louis, Missouri 63167, Estados Unidos de América, otorga poder a **EMILIO FERRERO, GONZALO PERDOMO, LUZ CLEMENCIA DE PAEZ Y GERMAN CAVELIER**). Dado y firmado el 21 de mayo de 2001 en St. Louis, MO, por Dennis R. Hoerner, Jr. (Firma ilegible).

CERTIFICADO NOTARIAL (SOCIEDAD) en inglés y español referente a la existencia legal de **MONSANTO TECHNOLOGY LLC**. Dado en la ciudad de St. Louis, Estado de Missouri, el 18 de mayo de 2001.

(Firma) Judith A. Lorenz, Notario Público. (Sello notarial en tinta) JUDITH A. LORENZ, Notario Público, Estado de Missouri,

Condado de St. Louis, Mi comisión expira el 20 de noviembre de

2003. (Sello seco de Judith A. Lorenz, Notario Público)



APOSTILLA

(Convención de La Haya del 5 de octubre de 1961)

1. País: Estados Unidos de América

Este documento público

2. Ha sido firmado por JUDITH A. LORENZ

3. Actuando en su capacidad de NOTARIO PÚBLICO

320

4. Lleva el sello/timbre de JUDITH A. LORENZ, NOTARIO PÚBLICO,
ESTADO DE MISSOURI

CERTIFICADO

5. En Jefferson City, Missouri.
6. el 29 de mayo de 2001
7. Por Matt Blunt, Secretario de Estado, Estado de Missouri.
8. No. 63157.
9. Sello: Sello del Secretario de Estado, Missouri.
10. Firma: (Firma) Matt Blunt.

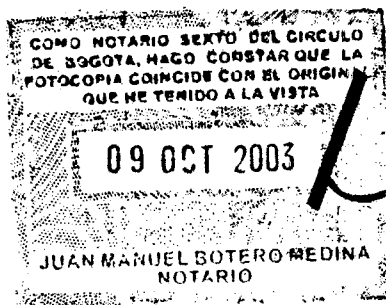
Es traducción fiel y completa de la cual se deja copia en esta
oficina para su confrontación.

WPC 12746-801-001-3

ID 3

JUN 12/01

Maria E. Martelo
TRADUCCION No: 1506/01
MARIA ELVIRA MARTELO
Traductora e Interprete Oficial
Inglés - Español - Inglés
Res. No. 2879 Min. Justicia



MINISTERIO DE RELACIONES
EXTERIORES
Quintero
331111
CUYA FIRMA APARECE EN EL
DOCUMENTO DESEMPEÑA
LAS FUNCIONES INDICADAS

NO SE ASUME
RESPONSABILIDAD DEL TEXTO
2001 JUN 12 A.M. 40
JEFE DE LEGATIZACIONES
SANTAFE DE BOGOTA D.C.

4

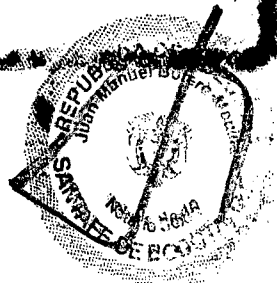
COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA(S) ANTERIOR(ES) FIRMA(S) PUESTA(S) POR: [Signature]

IDENTIFICADOS CON C.G. No.(s) _____

ES(SON) AUTENTICA(S) _____

SANTAFE DE BOGOTA, **12 JUN. 2001**

 DISEÑO 21415 CN-UN



COMO NOTARIO SEXTO DEL CIRCULO DE BOGOTA, HAGO CONSTAR QUE LA FOTOCOPIA COINCIDE CON EL ORIGINAL QUE HE TENIDO A LA VISTA

08 OCT 2003

JUAN MANUEL BOTERO MEDINA
NOTARIO

RECEIVED
NOTARIO
JUAN MANUEL BOTERO MEDINA
08 OCT 2003

Apostille

(Convention de La Haye du 5 Octobre 1961)

1. Country: United States of America

This public document:

2. has been signed by Harriet Smith Windsor

3. acting in the capacity of Secretary of State of Delaware

4. bears the seal/stamp of Office of Secretary of State

Certified

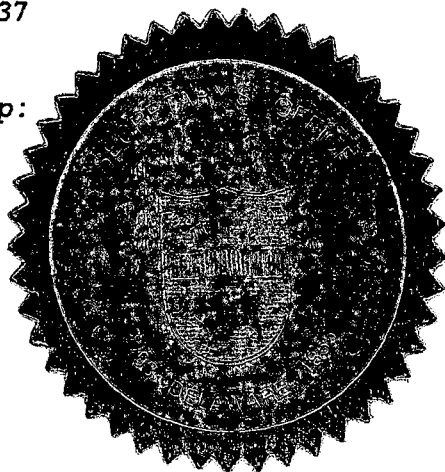
5. at Dover, Delaware

6. the eighth day of September, A.D. 2003

7. by Secretary of State, Delaware Department of State

8. No. 0209137

9. Seal/Stamp:



10. Signature:

Harriet Smith Windsor
Secretary of State

COMO NOTARIO SEYTO (E) DEL GOBIERNO
DE DELAWARE, HAYO CONFEERENCIADO LA
FOTOCOPIA CONSIDERANDO LA
DEBERANDO A LA LEY

17 OCT 2003

321
x6
328

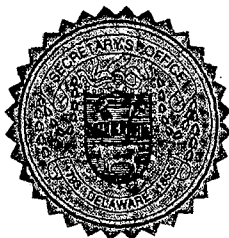
Delaware

PAGE 1

229 322

The First State

I, HARRIET SMITH WINDSOR, SECRETARY OF STATE OF THE STATE OF DELAWARE, DO HEREBY CERTIFY THE ATTACHED IS A TRUE AND CORRECT COPY OF THE CERTIFICATE OF AMENDMENT OF "MONSANTO COMPANY", CHANGING ITS NAME FROM "MONSANTO COMPANY" TO "PHARMACIA CORPORATION", FILED IN THIS OFFICE ON THE THIRTY-FIRST DAY OF MARCH, A.D. 2000, AT 2:15 O'CLOCK P.M.



0341113 8100

020316802

CONFIRMADO EN EL (2) DEL CIRCULO
DE ECONOMIA, HAGO CONSTAR QUE LA
REPRODUCCION ES FIDEL AL ORIGINAL
QUE HE TENIDO A LA VISTA

17 OCT 2003

Harriet Smith Windsor

Harriet Smith Windsor, Secretary of State

AUTHENTICATION: 1784045

DATE: 05-17-02

330
323

**CERTIFICATE OF AMENDMENT
OF
MONSANTO COMPANY
RESTATED CERTIFICATE OF INCORPORATION**

Monsanto Company (the "Corporation"), a corporation organized and existing under and by virtue of the General Corporation Law of the State of Delaware, does hereby certify that:

- I. The amendments set forth below to the Corporation's Restated Certificate of Incorporation previously filed in the Office of the Secretary of State of Delaware on October 29, 1997, have been duly adopted by the Board of Directors of the Corporation, and the Board has declared said amendments to be advisable and called a meeting of the stockholders of the Corporation for consideration thereof.
- II. Thereafter, pursuant to resolution of its Board of Directors, a special meeting of the stockholders of said corporation was duly called and held, upon notice in accordance with Section 222 of the General Corporation Law of the State of Delaware at which meeting the necessary number of shares as required by statute were voted in favor of the amendments.
- III.
 1. Article I thereof is amended and restated to read as follows:

ARTICLE I: NAME

The name of the Corporation shall be Pharmacia Corporation.

2. The first sentence of Article IV thereof is amended to read as follows:

The total number of shares of all classes of stock which the Corporation shall have authority to issue is 3,010,000,000 shares, to be divided into two classes consisting of (a) ten million (10,000,000) shares of preferred stock, par value \$.01 per share (hereinafter designated "Preferred Stock"), and (b) three billion (3,000,000,000) shares of common stock of a par value of \$2 per share (hereinafter designated "Common Stock").

3. The last sentence of the first paragraph of Article IV, Section I thereof is deleted.

4. Article IV, Section I(b) is amended and restated to read as follows:

STATE OF DELAWARE
SECRETARY OF STATE
DIVISION OF CORPORATIONS
FILED 02:15 PM 03/31/2000
001164549 - 0341113

RECORDED & INDEXED BY CLERK OF COURT
DEPARTMENT OF TREASURY
FILED IN OFFICE OF THE CLERK OF COURT
LA VISTA

17 OCT 2003

W/415979V1

FROM RICHARDS, LAYTON & FINGER #7

(FRI) 3.31'00 14:18/ST. 14:17/NO. 4862637689 P 4

227
324

(b) Whether the shares of such series shall have voting rights, in addition to the voting rights provided by law, and, if so, the terms of such voting rights;

- IV. These amendments were duly adopted in accordance with the provisions of Section 242 of the General Corporation Law of the State of Delaware.
- V. These amendments shall become effective as of 4:00 p.m. on March 31, 2000.

CONFESE EN EL CIRCULO
DE FUEGO EN LA CORDON QUE LA
FOTOCOPIA SE CONFESE CON EL ORIGINAL
QUE SE TIENEN A LA VISTA

17 OCT 2003

PAULO MENDEZ BARRUAS
NOTARIO (E)

FROM RICHARDS, LAYTON & FINGER #7

(FRI) 3.31'00 14:19/ST.14:17/NO.4862637689 P 5

325

IN WITNESS WHEREOF, Monsanto Company has caused this certificate to be signed
by Barbara L. Blackford, its authorized officer, this 31st day of March, 2000.

MONSANTO COMPANY

Barbara L. Blackford
Name: Barbara L. Blackford
Title: Assistant Secretary

17 OCT 2003
ADOLFO MENDEZ B. RAJAS
NOTARIO (B)

326
TRADUCCIÓN OFICIAL No. 10.10/02a realizada por Diego Vargas, Traductor
Oficial, Resolución No. 0001 de 1999 del Ministerio de Justicia y
registrado ante el Ministerio de Relaciones Exteriores de Colombia.

Delaware

PÁGINA 1

El Primer Estado

YO, HARRIET SMITH WINDSOR, SECRETARIO DE ESTADO DEL ESTADO DE
DELAWARE, POR EL PRESENTE CERTIFICO QUE LA ADJUNTA ES UNA COPIA FIEL
Y EXACTA DEL CERTIFICADO DE REFORMA DE "MONSANTO COMPANY" POR EL
CUAL SE CAMBIA SU NOMBRE DE "MOSANTO COMPANY" A "PHARMACIA
CORPORATION" PRESENTADO ANTE ESTA OFICINA EL TREINTA Y UNO DE MARZO
DE 2000 A LAS 2:15 P.M.



0341113 8100

020316802

Firma ilegible

Harriet Smith Windsor, Secretario de Estado

AUTENTICACIÓN: 1784045. CONFORME AL CERTIFICADO DEL SECRETARIO DEL ESTADO DEL DEPARTAMENTO DE AGRICULTURA Y GANADERÍA DEL ESTADO DE DELAWARE, EL CUAL CONSTA QUE LA COPIA QUE SE PRESENTA ES UNA COPIA FIEL Y EXACTA DEL ORIGINAL QUE SE ENCUENTRA EN LA OFICINA DEL SECRETARIO DE ESTADO.

FECHA 05-17-02 OCT 2003

CERTIFICADO DE REFORMA

DEL

CERTIFICADO DE CONSTITUCIÓN REPLANTEADO DE

MONSANTO COMPANY

257
327

Monsanto Company (la "Sociedad") una sociedad organizada y existente según y en virtud de la Ley General de Sociedades del Estado de Delaware, por el presente certifica que:

I. Las reformas planteadas a continuación al Certificado de Constitución Replanteado de la Sociedad, anteriormente presentado ante la oficina del Secretario de Estado de Delaware el 29 de octubre de 1997, han sido debidamente aprobadas por la Junta Directiva de la Sociedad, y la Junta ha declarado que dichas reformas son recomendables y ha convocado a una reunión de accionistas de la Sociedad para la consideración de las mismas.

II. Posteriormente, de acuerdo a una resolución de su Junta Directiva, una reunión especial de accionistas de dicha sociedad fue debidamente convocada y realizada, previa notificación en concordancia con la Sección 222 de la Ley General de Sociedades del Estado de Delaware, reunión en la cual el número necesario de acciones requerido por el estatuto votó a favor de las reformas.

III.

1. El Artículo I del mismo se modifica y replantea para que diga:

ARTÍCULO I: NOMBRE

El nombre de la Sociedad será Pharmacia Corporation

2. La primera oración del Artículo IV del mismo se modifica para que diga:

325
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El número total de acciones de todas las clases que la Sociedad estará autorizada a emitir es de 3,010,000,000 acciones las cuales estarán divididas en dos clases a saber (a) diez millones (10,000,000) de acciones preferenciales con valor nominal de \$.01 dólares por acción (en adelante llamado "Acciones Preferenciales") y (b) tres billones [Americanos] (3,000,000,000) de acciones ordinarias con valor nominal de \$2 dólares por acción (en adelante llamadas "Acciones Ordinarias").

3. La última oración del primer párrafo del Artículo IV, Sección I del mismo es eliminado.

4. Artículo IV, Sección I(b) se reforma y replantea para que diga lo siguiente:

ESTADO DE DELAWARE
SECRETARIO DE ESTADO
DIVISIÓN DE CORPORACIONES
PRESENTADO 02:15 PM 03/31/2000
001164549 - 0341113

(b) Ya sea que las acciones de dichas tengan derechos de voto, además de los derechos de voto establecidos por la ley, y si así fuere, los términos de dichos derechos de voto;

IV. Estas reformas fueron debidamente adoptadas en concordancia con las disposiciones de la Sección 242 de la Ley General de Sociedades del Estado de Delaware.

V. Estas reformas entrarán en vigencia a partir de las 4:00 p.m. del 31 de marzo de 2000.

EN TESTIMONIO DE LO CUAL, Monsanto Company ha ordenado que este certificado sea firmado por Barbara L. Blackford, su oficial autorizado, hoy 31 de Marzo de 2000.

MONSANTO COMPANY

Firma Ilegible

Nombre: Barbara L. Blackford

Cargo: Subsecretaria

Apostilla

(Convention de La Haye du 5 Octobre 1961)

1. País: Estados Unidos de América

Este documento público:

2. ha sido firmado por Harriet Smith Windsor

3. actuando en calidad de Secretario de Estado de Delaware

4. lleva el sello/estampilla de la Oficina del Secretario de Estado

Certificado

5. en Dover, Delaware

6. el ocho de Septiembre de 2003

7. por el Secretario de Estado, Departamento de Estado de Delaware

8. No. 0209137

9. Sello/estampilla:

10. Firma:



Harriet Smith Windsor

17 OCT 2003

Secretario de Estado

Es traducción fiel y completa de la cual se deja copia en esta oficina para su confrontación.

DVZ/ID-4919/WPCL002G/COLO 12746-803-001-1

DIEGO F. VARGAS Z.

TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA(S) ANTERIOR(ES) FIRMA(S) PUESTA(S) POR

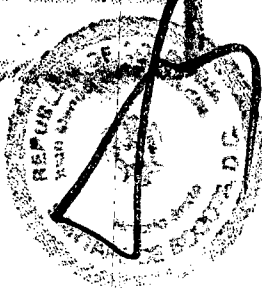
Diego Vargas

IDENTIFICADOS CON C.C. No(s)

ES(SON) AUTENTICA(S)

SANTAFE DE BOGOTA, 16 OCT. 2003





NO GLASUNE
17 OCT 16 PM 1:30

2003 OCT 16 PM 1:30

Diego Vargas
NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA

MINISTERIO DE JUSTICIA

490057

Diego Vargas

NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA

COMO NOTARIO SEXTO DEL CIRCULO DE SANTAFE DE BOGOTA, HAGO CONSTAR QUE LA(S) ANTERIOR(ES) FIRMA(S) PUESTA(S) POR

Diego Vargas

IDENTIFICADOS CON C.C. No(s)

ES(SON) AUTENTICA(S)

SANTAFE DE BOGOTA, 17 OCT. 2003



Diego Vargas

#330
25

Apostille

(Convention de La Haye du 5 octobre 1961)

1. Country: United States of America

- This public document
2. has been signed by MICHELLE LUDWIG
3. acting in the capacity of NOTARY PUBLIC
4. bears the seal/stamp of MICHELLE LUDWIG-NOTARY PUBLIC-STATE OF MISSOURI

Certified

5. at Jefferson City, Missouri
6. the 12th day of SEPTEMBER, 2003
7. by Matt Blunt, Secretary of State, State of Missouri
8. No. 95283
9. Seal/Stamp
10. Signature:

Matt Blunt

Comm. 48 (12-2000)

COMO NOTARIO SEXTO (S) DEL CIRCUITO
DE BOGOTA, HAGO CONSTAR QUE LA
COPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA

17 OCT 2003

Apostille

(Convention de La Haye du 5 Octobre 1961)

331

25

1. Country: **United States of America**

This public document

2. has been signed by **Gloria D'Amico**

3. acting in the capacity of **County Clerk**

4. bears the seal/stamp of the county of **Queens**

Certified

5. At New York, New York 6. the 10th day of September 2003

7. by Special Deputy Secretary of State, State of New York

8. No. NYC-10083722B

9. Seal/Stamp

10. Signature

James Bizzarri

James Bizzarri

Special Deputy Secretary of State

COMO NOTARIO DE LA LEY DEL CIRCULO
DE BOGOTA, NO PUEDO MONSTRAR QUE LA
FOTOCOPIA CONCORDA CON EL ORIGINAL
QUE ME FUE PRESENTADO A LA VISTA

17 OCT 2003

ALBERTO GARCIA JAS
NOTARIO

224
332

State of New York } ss.:
County of Queens }

Nº 78916

Form 1

I, GLORIA D'AMICO, Clerk of the County of Queens, and Clerk of the Supreme Court in and for said county the same being a court of record having a seal, DO HEREBY CERTIFY THAT

Rosalba Oliveri

whose name is subscribed to the annexed original instrument has been commissioned and qualified as a NOTARY PUBLIC.



and has filed his autograph signature in this office and that he/she was at the time of taking such proof or acknowledgment or oath duly authorized by the laws of the State of New York to take the same; that he is well acquainted with the handwriting of such public officer or has compared the signature on the certificate of proof or acknowledgment or oath with the autograph signature filed in his office by such public officer, and he believes that the signature on the original instrument is genuine.

IN WITNESS WHEREOF, I have hereunto set my hand and my official seal this

day of SEP - 9 2003

Gloria D'Amico
County Clerk, Queens County

COMO NOTARIO DEL CÍRCULO
DE LOSA Y C. CONSTAR QUE LA
FOTOCOPIA ES VERDADERA CON EL ORIGINAL
QUE SE PRESENTA A LA VISTA

17 OCT 2003

[Signature]
PABLO RENDEZ PARAJAS
NOTARIO

340
333

STATE OF New York §
COUNTY OF New York § ss.
§

SUBSCRIBED AND SWORN BEFORE ME, the undersigned authority, on this 21 day of August, 2003, personally appeared J. Trevor Lumb, known to me to be the person whose name is subscribed to the foregoing instrument on behalf of Pharmacia Corporation (formerly Monsanto Company), and acknowledged to me that he is authorized to validly sign alone such an assignment on behalf of said company.

Rosalba Oliveri
Notary
ROSALBA OLIVERI
Notary Public, State of New York
No. 01OL6085628
Qualified in Queens County
Certificate Filed in New York County
Commission Expires December 30, 2006

STATE OF MISSOURI §
COUNTY OF ST. LOUIS § ss.
§

SUBSCRIBED AND SWORN BEFORE ME, the undersigned authority, on this 29 day of August, 2003, personally appeared Thomas P. McBride, known to me to be the person whose name is subscribed to the foregoing instrument on behalf of Monsanto Technology LLC, and acknowledged to me that he is authorized to validly sign alone such an assignment on behalf of said company.

Michelle Ludwig
Notary



[Handwritten signature]

NOTARIO PUBLICO (P) DEL CIRCULO
DE MONTEVIDEO, HAGO CONSTAR QUE LA
COPIA CONFORME CON EL ORIGINAL
QUE ME FUE PRESENTADO A LA VISTA

17 OCT 2003

DOCUMENT OF ASSIGNMENT OF
PATENT

ASSIGNMENT

The undersigned **Pharmacia Corporation**,
(formerly Monsanto Company, by virtue of a
certificate of name change dated March 31,
2000)

acting as a corporation

of Delaware, U.S.A.

with domicile in

800 North Lindbergh Boulevard
St. Louis, Missouri 63167, U.S.A.

hereby declares that it assigns all rights of
ownership as well as all rights and privileges
relating thereto without exception over the
following patents of invention in Colombia:

Application No. 29094;

Application No. 29094A;

and Application No. 29094B

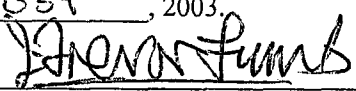
to **Monsanto Technology LLC**

domiciled in

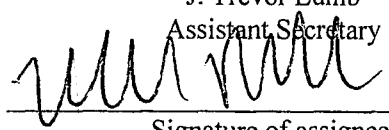
800 North Lindbergh Boulevard
St. Louis, Missouri 63167, U.S.A.

The assignor and the assignee sign this
document as proof of their acceptance of the
assignment.

Given and signed on the 21 day of
August, 2003.


Signature of assignor,
PHARMACIA CORPORATION

J. Trevor Lumb
Assistant Secretary


Signature of assignee,
MONSANTO TECHNOLOGY LLC
Thomas P. McBride
Deputy Associate General Counsel - IP

Notarization and Legalization Required

DOCUMENTO DE TRASPASO DE
PATENTE

CESION

El suscrito **Pharmacia Corporation** (anterior-
mente conocido como **Monsanto Company**, por
medio de un certificado de cambio de nombre
en calidad de **fechado 31 marzo, 2000**)

de **Delaware, EEUU**

con domicilio en

800 North Lindbergh Boulevard
St. Louis, Missouri 63167 EEUU

declara por el presente documento que cede
todos los derechos de propiedad que le
correspondan, así como las prerrogativas, sin
excepción alguna, sobre la siguiente patente de
invención en Colombia:

Solicitud No. 29094 ✓

Solicitud No. 29094A

Solicitud No. 29094B

a

Monsanto Technology LLC

domiciliada en

800 North Lindbergh Boulevard

St. Louis, Missouri 63167 EEUU

El cedente y el cesionario firman este
documento como prueba de su aceptación de
la cesión.

Dado y firmado a los 21 días del
mes de Agosto de 2003.

Firma del cedente

Firma del cesionario

17 OCT 2003

PAULO MENDEZ SARRAJAS
NOTARIO (C)

342
335

TRADUCCIÓN OFICIAL No 10.10/03b realizada por Diego Vargas, Traductor Oficial, Resolución No. 0001 de 1999 del Ministerio de Justicia y registrado ante el Ministerio de Relaciones Exteriores de Colombia.

A continuación se traducen los sellos y legalizaciones de un documento de Traspaso de Patente escrito en inglés y español por medio del cual Pharmacia Corporation (anteriormente conocida como Monsanto Company), una sociedad de Delaware, con domicilio en 800 North Lindbergh Boulevard, St. Louis, Missouri 63167, Estados Unidos de América cede las siguientes solicitudes de patente en Colombia: Solicitud No. 29094, Solicitud No. 29094A y Solicitud No. 29024B a la compañía **MONSANTO TECHNOLOGY LLC** domiciliada en el 800 North Lindbergh Boulevard, St. Louis, Missouri 63167, Estados Unidos de América.

Dado y firmado el 21 de agosto de 2003.

<u>Firma Ilegible</u>	<u>Firma Ilegible</u>
Firma del Cedente	Firma del Cesionario
PHARMACIA CORPORATION	MONSANTO TECHNOLOGY LLC
J. Trevor Lumb	Thomas P. McBride
Subsecretario	Asesor Legal General Asociado Suplente - PI

ESTADO DE Nueva York §
CONDADO DE Nueva York §

§ Declaración Juramentada 17 OCT 2003

SUSCRITO Y JURAMENTADO ANTE MÍ, la suscrita autoridad, hoy 21 de Agosto de 2003, personalmente compareció J. Trevor Lumb, quien sé que fue la persona cuyo nombre está suscrito en el anterior instrumento a nombre de Pharmacia Corporation (anteriormente

Monsanto Company), y reconoció ante mí que él está debidamente
autorizado para firmar solo dicha cesión a nombre de dicha compañía.

Firma Ilegible

Notario

ROSALBA OLIVERI
Notario Público, Estado de Nueva York
No.010L6085628
Calificado en el Condado de Queens
Certificado Presentado en el Condado de Nueva York
Mí Comisión Vence Diciembre 30 de 2006

(Anexo)

Estado de Nueva York,) **78916** Forma 1
Condado de Nueva York) Declaración Juramentada

Yo, GLORIA D'AMICO, Secretario del Condado de Queens y
Secretario de la Corte Suprema en y para dicho condado, siendo el
mismo un tribunal de registro que tiene por ley un sello, POR EL
PRESENTE CERTIFICO QUE

Rosalba Oliveri

cuyo nombre está suscrito en el anexo instrumento original ha sido
comisionada y calificada como NOTARIO PÚBLICO

y ha presentado su firma autógrafa en esta oficina y que al momento
de tomar dicha prueba o reconocimiento o juramento, él/ella estaba
debidamente autorizada por las leyes del Estado de Nueva York para
tomar los mismos; que él está bien familiarizado con la escritura de
dicho funcionario público o ha comparado la firma que aparece en el
certificado de prueba o reconocimiento o juramento con la firma
autógrafa presentada ante esta oficina por dicho funcionario público
y él considera que la firma en el documento original es auténtica.

EN TESTIMONIO DE LO CUAL, he firmado y colocado mí sello oficial al
presente hoy

SEP 9 DE 2003

Firma ilegible

Secretario de Condado, Condado de Queens

Apostilla

(Convention de La Haye du 5 Octobre 1961)

1. País: Estados Unidos de América

Este documento público

2. ha sido firmado por Gloria D'Amico

3. actuando en calidad de Secretario de Condado

4. lleva el sello/estampilla del condado de Queens

Certificado:

5. en Nueva York, Nueva York 6. el 10 de Septiembre de 2003

7. por el Suplente Especial del Secretario de Estado, Estado de Nueva York

8. NO. NYC-10083722B

9. Sello/estampilla:

10. Firma:



Diego F. Vargas
DIEGO F. VARGAS
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA

Firma ilegible

James Bizzarri

Suplente Especial del Secretario de Estado

17 OCT 2003

ESTADO DE MISSOURI

§

CONDADO DE SAN LOUIS

§ Declaración Juramentada

§

SUSCRITO Y JURAMENTADO ANTE MÍ, la suscrita autoridad, hoy 29 de Agosto de 2003, personalmente compareció Thomas P. McBride, quien sé que fue la persona cuyo nombre está suscrito en el anterior instrumento a nombre de Monsanto Technology LLC, y reconoció ante mí

que él está debidamente autorizado para firmar solo dicha cesión a nombre de dicha compañía.

Firma Ilegible

Notario

MICHELLE LUDWIG
Condado de San Louis
Mí Comisión Vence
Julio 13 de 2005

Apostilla

(Convention de La Haye du 5 octobre 1961)

1. País: Estados Unidos de América

Este documento público

2. ha sido firmado por MICHELLE LUDWIG

3. actuando en capacidad de NOTARIO PÚBLICO

4. lleva el sello/estampilla de MICHELLE LUDWIG - NOTARIO PÚBLICO - ESTADO DE MISSOURI

Certificado

5. En Jefferson City, Missouri

6. El 12 de SEPTIEMBRE de 2003

7. por Matt Blunt, Secretario de Estado, Estado de Missouri

8. No. 95283

9. Sello/estampilla:

10. Firma:

SELLO DEL SECRETARIO DE ESTADO

MISSOURI

17 OCT 2003
Matt Blunt

Es traducción fiel y completa de la cual se deja copia en esta oficina para su confrontación.

DYZ/ID-4921/WPCL002G/COLO 12746-803-001-1

Diego F. Vargas
DIEGO F. VARGAS
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA

25-

COMO NOTARIO SEXTO DEL CIRCULO DE SANTA FE DE BOGOTA, HAGO CONSTAR QUE LA(S) ANTERIOR(ES) FIRMA(S) PUESTA(S) POR

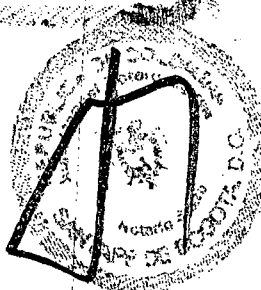
Diego Vargas

IDENTIFICADOS CON C.C. NO.(S)

ES(SON) AUTENTICA(S)

SANTA FE DE BOGOTA, 15 OCT-2003

 CODEX JURIS CIVILIS



NO SE ASUME
RESPONSABILIDAD DEL 1970

2003 OCT 16 P 1:40

Diego Vargas
NOTARIO PUBLICO
CIRCULO DE SANTA FE DE BOGOTA, D.C.

MINISTERIO DE ECONOMIA

1190448

Diego Vargas

COMO NOTARIO SEXTO DEL CIRCULO DE SANTA FE DE BOGOTA, HAGO CONSTAR QUE LA FIRMA PUESTA POR EL SEÑOR Diego Vargas CON EL ORIGINAL QUE ME FUE PRESENTADO A LA VISTA

15 OCT 2003

Diego Vargas

NOTARIO PUBLICO
CIRCULO DE SANTA FE DE BOGOTA, D.C.

339

SUPERINDUSTRIA Y COMERCIO
Radicacion : 00023094 00000005 Folios: 27
Fecha (ARM): 2003-10-21 17:40:34
Tramite : 002 PATENTES D 1 REGISTRO/ 329 COMPLEMEN
NIT : 000170007 2 Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

RECIBO OFICIAL DE CAJA : 03 - 75,097
FECHA : OCTUBRE 15 DE 2003

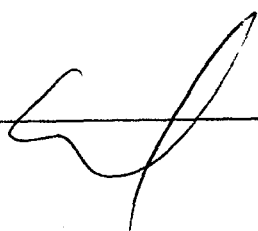
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	Nº. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ASSOCADOS	CONSIGNACION	BANCO POPULAR	050-00110-L	15531373	15/10/2003	20,481,000.00

***** CONCEPTO *****

CANT. RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-03 CAMBIO DE MODALIDAD Y MODIFICA	12 MARCAS Y LENAS COMERCIALES	82,000.00
	TOTAL :	\$ 82,000.00

CON: OCHENTA Y DOS MIL PESOS

RESPONSABLE : 
RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

12746-803-001-1

347/340

SUPERINDUSTRIA Y COMERCIO
Radicacion : 00029094 00000005 Folios: 27
Fecha (AMD): 2003-10-21 17:40:34
Tramite : 002 PATENTES D 1 REGISTRO/ 329 COMPLEMEN
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 03 - 72,732
FECHA : OCTUBRE 7 DE 2003

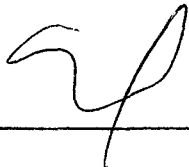
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	15534377	07/10/2003	37,381,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03	CAMBIO DE MODALIDAD Y MODIFICA	
12		MARCAS Y LEMAS COMERCIALES	82,000.00
		TOTAL :	\$ 82,000.00

SON: OCHENTA Y DOS MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

010 12482-805-001-1

Exp. 00-29094 (A4B)

348341



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 25/30, 57/20, 25/08, 25/04	A1	(11) International Publication Number: WO 98/17109 (43) International Publication Date: 30 April 1998 (30.04.98)
(21) International Application Number: PCT/US97/19329 (22) International Filing Date: 24 October 1997 (24.10.97) (30) Priority Data: 60/029,317 25 October 1996 (25.10.96) US 60/034,887 31 January 1997 (31.01.97) US 60/039,789 4 March 1997 (04.03.97) US (71) Applicant: MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US). (72) Inventors: GILLESPIE, Jane, L.; 7229 Cornell, St. Louis, MO 63130 (US). WARD, Anthony, J., I.; 821 Westwood Drive, Clayton, MO 63105 (US). (74) Agent: GOODMAN, Kenneth, D.; Arnold, White & Durkee, P.O. Box 4433, Houston, TX 77210 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: COMPOSITION AND METHOD FOR TREATING PLANTS WITH EXOGENOUS CHEMICALS

(57) Abstract

Methods and compositions are disclosed wherein exogenous chemicals are applied to plants to generate a desired biological response. One embodiment of the present invention is a plant treatment composition that comprises (a) an exogenous chemical and (b) an alkylether surfactant or mixture of such surfactants having the formula $R^{12}-O-(CH_2CH_2O)_n(CH(CH_3)CH_2O)_m-R^{13}$ wherein R^{12} is an alkyl or alkenyl group having about 16 to about 22 carbon atoms, n is an average number of about 10 to about 100, m is an average number of 0 to about 5 and R^{13} is hydrogen or C_{1-4} alkyl. The alkylether surfactant or mixture thereof is present in an amount such that the weight/weight ratio of said alkylether surfactant or mixture of such surfactants to the exogenous chemical is about 1:3 to about 1:100.

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COMPOSITION AND METHOD FOR TREATING PLANTS WITH
EXOGENOUS CHEMICALS

BACKGROUND OF THE INVENTION

5 This invention relates to formulations and methods for enhancing the efficacy of exogenous chemicals used in treating plants. An exogenous chemical, as defined herein, is any chemical substance, whether naturally or synthetically derived, which (a) has biological activity or is capable of releasing in a plant an ion, moiety or derivative which has biological activity, and (b) is applied to a plant with the intent or result that the chemical substance or its biologically active ion, moiety or derivative enter living
10 cells or tissues of the plant and elicit a stimulatory, inhibitory, regulatory, therapeutic, toxic or lethal response in the plant itself or in a pathogen, parasite or feeding organism present in or on the plant. Examples of exogenous chemical substances include, but are not limited to, chemical pesticides (such as herbicides, algicides, fungicides, bactericides, viricides, insecticides, aphicides, miticides, nematocides, molluscicides, and the like), plant growth regulators, fertilizers and nutrients, gametocides, defoliants,
15 desiccants, mixtures thereof, and the like.

 Exogenous chemicals, including foliar-applied herbicides, have at times been formulated with surfactants, so that when water is added, the resulting sprayable composition is more easily and effectively retained on the foliage (e.g., the leaves or other photosynthesizing organs) of plants. Surfactants can also bring other benefits, including improved contact of spray droplets with a waxy leaf
20 surface and, in some cases, improved penetration of the accompanying exogenous chemical into the interior of leaves. Through these and perhaps other effects, surfactants have long been known to increase the biological effectiveness of herbicide compositions, or other compositions of exogenous chemicals, when added to or included in such compositions. Thus, for example, the herbicide glyphosate (N-phosphonomethylglycine) has been formulated with surfactants such as polyoxyalkylene-type surfactants /
25 including, among other surfactants, polyoxyalkylene alkylamines. Commercial formulations of glyphosate herbicide marketed under the trademark ROUNDUP® have been formulated with a surfactant composition based on such a polyoxyalkylene alkylamine, in particular a polyethoxylated tallowamine, this surfactant composition being identified as MON 0818. Surfactants have generally been combined with glyphosate or other exogenous chemicals either in a commercial concentrate (herein referred to as a
30 "coformulation"), or in a diluted mixture that is prepared from separate compositions, one comprising an exogenous chemical (e.g. glyphosate) and another comprising surfactant, prior to use in the field (i.e., a tank mix).

 Various combinations of exogenous chemicals and surfactants or other adjuvants have been tested in the past. In some instances, the addition of a particular surfactant has not produced uniformly
35 positive or negative changes in the effect of the exogenous chemical on the plant (e.g., a surfactant that

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may enhance the activity of a particular herbicide on certain weeds may interfere with, or antagonize, the herbicidal efficacy on another weed species).

Some surfactants tend to degrade fairly rapidly in aqueous solutions. As a result, surfactants that exhibit this property can only be used effectively in tank mixes (i.e., mixed with the other ingredients in solution or dispersion in the tank soon before spraying is to occur), rather than being coformulated in an aqueous composition with the other ingredients in the first instance. This lack of stability, or inadequate shelf-life, has hindered the use of certain surfactants in some exogenous chemical formulations.

Other surfactants, though chemically stable, are physically incompatible with certain exogenous chemicals, particularly in concentrate coformulations. For example, most classes of nonionic surfactant, including polyoxyethylene alkylether surfactants, do not tolerate solutions of high ionic strength, as for example in a concentrated aqueous solution of a salt of glyphosate. Physical incompatibility can also lead to inadequate shelf-life. Other problems that can arise from such incompatibility include the formation of aggregates large enough to interfere with commercial handling and application, for example by blocking spray nozzles.

Another problem that has been observed in the past is the effect of environmental conditions on uptake of an exogenous chemical composition into foliage of a plant. For example, conditions such as temperature, relative humidity, presence or absence of sunlight, and health of the plant to be treated, can affect the uptake of a herbicide into the plant. As a result, spraying exactly the same herbicidal composition in two different situations can result in different herbicidal control of the sprayed plants.

One consequence of the above-described variability is that often a higher rate of herbicide per unit area is applied than might actually be required in that situation, in order to be certain that adequate control of undesired plants will be achieved. For similar reasons, other foliar-applied exogenous chemicals are also typically applied at significantly higher rates than needed to give the desired biological effect in the particular situation where they are used, to allow for the natural variability that exists in efficiency of foliar uptake. A need therefore exists for compositions of exogenous chemicals that, through more efficient uptake into plant foliage, allow reduced use rates.

Many exogenous chemicals are commercially packaged as a liquid concentrate that contains a significant amount of water. The packaged concentrate is shipped to distributors or retailers. Ultimately the packaged concentrate ends up in the hands of an end user, who further dilutes the concentrate by adding water in accordance with label instructions on the package. The dilute composition thus prepared is then sprayed on plants.

A significant portion of the cost of such packaged concentrates is the cost of transporting the concentrate from the manufacturing site to the location where the end user purchases it. Any liquid concentrate formulation that contained relatively less water and thus more exogenous chemical would reduce the cost per unit amount of exogenous chemical. However, one important limit on the ability of the manufacturer to increase the loading of the exogenous chemical in the concentrate is the stability of

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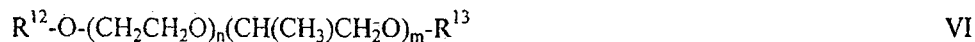
that formulation. With some combinations of ingredients, a limit will be reached at which any further reduction of water content in the concentrate will cause it to become unstable (e.g., to separate into discrete layers), which may make it commercially unacceptable.

Accordingly, a need exists for improved formulations of exogenous chemicals, particularly herbicides, that are stable, effective, less sensitive to environmental conditions, and permit the use of reduced amounts of exogenous chemical to achieve the desired biological effect in or on plants. A need also exists for stable liquid concentrate formulations of exogenous chemicals that contain less water and more exogenous chemical than prior art concentrates.

SUMMARY OF THE INVENTION

The present invention relates to novel methods and compositions wherein exogenous chemicals are applied to plants to generate a desired biological response.

One embodiment of the present invention is a plant treatment composition that comprises (a) an exogenous chemical and (b) an alkylether surfactant or mixture of such surfactants having the formula



wherein R^{12} is an alkyl or alkenyl group having about 16 to about 22 carbon atoms, n is an average number of about 10 to about 100, m is an average number of 0 to about 5 and R^{13} is hydrogen or C_{1-4} alkyl. The alkylether surfactant or mixture thereof is present in an amount such that the weight/weight ratio of said alkylether surfactant or mixture of such surfactants to the exogenous chemical is about 1:3 to about 1:100. The term "alkylether" as used herein should be understood to include alkenylether surfactants. Preferably R^{12} is a saturated straight-chain alkyl group, R^{13} is hydrogen, m is 0 and n is from about 10 to about 40, more preferably from about 20 to about 40. Most preferably the alkylether surfactant is a polyoxyethylene cetyl or stearyl ether or mixture thereof having 20-40 moles of ethylene oxide (EO).

In one embodiment, the composition is an aqueous concentrate further comprising water and an amount of a solid inorganic particulate colloidal material effective to stabilize the composition, said composition not exhibiting phase separation over a period of time T as defined below when stored in a closed container at a temperature in the range from about 15°C to about 30°C; wherein the exogenous chemical and the surfactant are present at concentrations in the absolute or relative to each other such that, in the absence of the colloidal material, phase separation would occur during said period of time T .

The period of time T over which a composition can be observed to determine if phase separation occurs is in the range from about 1 hour to about 60 days. "Phase separation" in the present context means separation of at least part of the surfactant component from other ingredients of the composition as a distinct phase. The particulate colloidal material preferably is present in an amount between about 0.01% and about 5% by weight, more preferably between about 0.5% and about 2.5% by weight, of the composition. By "aqueous concentrate" is meant a composition comprising water and from about 10% to about 60% by weight of the exogenous chemical.

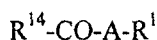
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Examples of suitable solid particulate colloidal materials include inorganic oxides such as silicon oxides, aluminum oxides, titanium oxides, and mixtures thereof. Preferably the particulate colloidal material has an average specific surface area of about 50 to about 400 m²/g, more preferably about 180 to about 400 m²/g. In one particular embodiment, the particulate colloidal material has a bimodal

5 distribution of specific surface area whereby a first component of the colloidal material has an average specific surface area of about 50 to about 150 m²/g and a second component of the colloidal material has an average specific surface area of about 180 to about 400 m²/g.

In another embodiment of the invention, compositions are provided comprising (a) an exogenous chemical, (b) an alkylether surfactant or mixture of such surfactants having the formula shown above,

10 and (c) a compound of formula



VII

wherein R¹⁴ is a hydrocarbyl group having about 5 to about 21 carbon atoms, R¹⁵ is a hydrocarbyl group having 1 to about 14 carbon atoms, the total number of carbon atoms in R¹⁴ and R¹⁵ is about 11 to about 27, and A is O or NH. R¹⁴ preferably has about 11 to about 21 carbon atoms, R¹⁵ preferably has 1 to

15 about 6 carbon atoms and A is preferably O. The aqueous composition in embodiments comprising a compound of formula VII preferably is an emulsion comprising an oil phase that comprises said second excipient substance, for example a water-in-oil-in-water multiple emulsion or an oil-in-water emulsion.

A composition comprising a compound of formula VII can, if desired or necessary, further comprise an amount of solid inorganic particulate colloidal material effective to stabilize the composition, exactly as defined above.

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In certain preferred embodiments of the present invention, the compound (c) is a C₁₋₄ alkyl ester of a C₁₂₋₁₈ fatty acid, more preferably a C₁₋₄ alkyl ester of a C₁₂₋₁₈ saturated fatty acid. Propyl, isopropyl or butyl esters of C₁₂₋₁₈ fatty acids, such as butyl stearate, are especially preferred.

A wide variety of exogenous chemicals can be used in the compositions and methods of the present invention. A preferred class is foliar-applied exogenous chemicals, i.e. exogenous chemicals that are normally applied post-emergence to foliage of plants. A preferred subclass of foliar-applied exogenous chemicals is those that are water-soluble. By "water-soluble" in this context is meant having a solubility in distilled water at 25°C greater than about 1% by weight. Especially preferred water-soluble exogenous chemicals are salts that have an anion portion and a cation portion. In one

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30 embodiment of the invention, at least one of the anion and cation portions is biologically active and has a molecular weight of less than about 300. Particular examples of such exogenous chemicals where the cation portion is biologically active are paraquat, diquat and chlormequat. More commonly it is the anion portion that is biologically active.

Another preferred subclass of exogenous chemicals is those that exhibit systemic biological activity in the plant. Within this subclass, an especially preferred group of exogenous chemicals is N-phosphonomethylglycine and its herbicidal derivatives. N-phosphonomethylglycine, often referred to by

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preferably at least about 15%.

The compositions and methods of the present invention have a number of advantages. They provide enhanced biological activity of exogenous chemicals in or on plants in comparison with prior formulations, either in terms of greater ultimate biological effect, or obtaining an equivalent biological effect while using a reduced application rate of exogenous chemical. Certain herbicide formulations of the present invention can avoid antagonism that has been observed in some prior art herbicide formulations, and can minimize quick production of necrotic lesions on leaves that in some situations hinder overall translocation of herbicide in the plant. Certain herbicide compositions of the invention modify the spectrum of activity of the herbicide across a range of plant species. For example, certain formulations of the present invention containing glyphosate can provide good herbicidal activity against broadleaf weeds while not losing any herbicidal effectiveness on narrowleaf weeds. Others can enhance herbicidal effectiveness on narrowleaf weeds to a greater extent than on broadleaf weeds. Still others can have enhanced effectiveness which is specific to a narrow range of species or even a single species.

Another advantage of the present invention is that it employs relatively small amounts of the alkylether surfactant in relation to the amount of exogenous chemical employed. This makes the compositions and methods of the present invention relatively inexpensive, and also tends to reduce instability problems in specific compositions where the alkylether surfactant is physically incompatible with the exogenous chemical (e.g., in solutions of high ionic strength, such as concentrated glyphosate salt solutions).

Even at the low concentrations of the excipient substances used in the present invention, there may be limits on the maximum concentration of exogenous chemical that can be used without causing compatibility problems (e.g., separation of the composition into discrete layers). In some preferred embodiments of the invention, composition stability at high loadings of exogenous chemical is maintained by adding other ingredients such as, for example, colloidal particulates. Some compositions of the present invention exhibit enhanced biological activity and have a higher loading of exogenous chemical than possible in prior art compositions.

Further, compositions of the present invention are less sensitive in some instances to environmental conditions such as relative humidity at the time of application to the plant. Also, the present invention allows the use of smaller amounts of herbicides or other pesticides, while still obtaining the required degree of control of weeds or other undesired organisms.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

Examples of exogenous chemical substances that can be included in compositions of the present invention include, but are not limited to, chemical pesticides (such as herbicides, algicides, fungicides, bactericides, viricides, insecticides, aphicides, miticides, nematocides, molluscicides and the like), plant growth regulators, fertilizers and nutrients, gametocides, defoliants, desiccants, mixtures thereof and the like. In one embodiment of the invention, the exogenous chemical is polar.

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A preferred group of exogenous chemicals are those that are normally applied post-emergence to the foliage of plants, i.e. foliar-applied exogenous chemicals.

Some exogenous chemicals useful in the present invention are water-soluble, for example salts that comprise biologically active ions, and also comprise counterions, which may be biologically inert or relatively inactive. A particularly preferred group of these water-soluble exogenous chemicals or their biologically active ions or moieties are systemic in plants, that is, they are to some extent translocated from the point of entry in the foliage to other parts of the plant where they can exert their desired biological effect. Especially preferred among these are herbicides, plant growth regulators and nematocides, particularly those that have a molecular weight, excluding counterions, of less than about 300. More especially preferred among these are exogenous chemical compounds having one or more functional groups selected from amine, carboxylate, phosphonate and phosphinate groups.

Among such compounds, an even more preferred group are herbicidal or plant growth regulating exogenous chemical compounds having at least one of each of amine, carboxylate, and either phosphonate or phosphinate functional groups. Salts of N-phosphonomethylglycine are examples of this group of exogenous chemicals. Further examples include salts of glufosinate, for instance the ammonium salt (ammonium DL-homoalanin-4-yl (methyl) phosphinate).

Another preferred group of exogenous chemicals which can be applied by the method of the invention are nematocides such as those disclosed in U.S. Patent No. 5,389,680, the disclosure of which is incorporated herein by reference. Preferred nematocides of this group are salts of 3,4,4-trifluoro-3-butenic acid or of N-(3,4,4-trifluoro-1-oxo-3-butenyl)glycine.

Exogenous chemicals which can usefully be applied by the method of the present invention are normally, but not exclusively, those which are expected to have a beneficial effect on the overall growth or yield of desired plants such as crops, or a deleterious or lethal effect on the growth of undesirable plants such as weeds. The method of the present invention is particularly useful for herbicides, especially those that are normally applied post-emergence to the foliage of unwanted vegetation.

Herbicides which can be applied by the method of the present invention include but are not limited to any listed in standard reference works such as the "Herbicide Handbook," Weed Science Society of America, 1994, 7th Edition, or the "Farm Chemicals Handbook," Meister Publishing Company, 1997 Edition. Illustratively these herbicides include acetanilides such as acetochlor, alachlor and metolachlor, aminotriazole, asulam, bentazon, bialaphos, bipyridyls such as paraquat, bromacil, cyclohexenones such as clethodim and sethoxydim, dicamba, diflufenican, dinitroanilines such as pendimethalin, diphenylethers such as acifluorfen, fomesafen and oxyfluorfen, fatty acids such as C₉₋₁₀ fatty acids, fosamine, flupoxam, glufosinate, glyphosate, hydroxybenzonitriles such as bromoxynil, imidazolinones such as imazaquin and imazethapyr, isoxaben, norflurazon, phenoxies such as 2,4-D, phenoxypropionates such as diclofop, fluazifop and quizalofop, picloram, propanil, substituted ureas such as fluometuron and isoproturon, sulfonylureas such as chlorimuron, chlorsulfuron, halosulfuron,

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metsulfuron, primisulfuron, sulfometuron and sulfosulfuron, thiocarbamates such as triallate, triazines such as atrazine and metribuzin, and triclopyr. Herbicidally active derivatives of any known herbicide are also within the scope of the present invention. A herbicidally active derivative is any compound which is a minor structural modification, most commonly but not restrictively a salt or ester, of a known herbicide. These compounds retain the essential activity of the parent herbicide, but may not necessarily have a potency equal to that of the parent herbicide. These compounds may convert to the parent herbicide before or after they enter the treated plant. Mixtures or coformulations of a herbicide with other ingredients, or of more than one herbicide, may likewise be employed.

An especially preferred herbicide is N-phosphonomethylglycine (glyphosate), a salt, adduct or ester thereof, or a compound which is converted to glyphosate in plant tissues or which otherwise provides glyphosate ion. Glyphosate salts that can be used according to this invention include but are not restricted to alkali metal, for example sodium and potassium, salts; ammonium salt; alkylamine, for example dimethylamine and isopropylamine, salts; alkanolamine, for example ethanolamine, salts; alkylsulfonium, for example trimethylsulfonium, salts; sulfoxonium salts; and mixtures thereof. The herbicidal compositions sold by Monsanto Company as ROUNDUP® and ACCORD® contain the monoisopropylamine (IPA) salt of N-phosphonomethylglycine. The herbicidal compositions sold by Monsanto Company as ROUNDUP® Dry and RIVAL® contain the monoammonium salt of N-phosphonomethylglycine. The herbicidal composition sold by Monsanto Company as ROUNDUP® Geoforce contains the monosodium salt of N-phosphonomethylglycine. The herbicidal composition sold by Zeneca as TOUCHDOWN® contains the trimethylsulfonium salt of N-phosphonomethylglycine. The herbicidal properties of N-phosphonomethylglycine and its derivatives were first discovered by Franz, then disclosed and patented in U.S. Patent 3,799,758, issued March 26, 1974. A number of herbicidal salts of N-phosphonomethylglycine were patented by Franz in U.S. Patent 4,405,531, issued September 20, 1983. The disclosures of both of these patents are hereby incorporated by reference.

Because the commercially most important herbicidal derivatives of N-phosphonomethylglycine are certain salts thereof, the glyphosate compositions useful in the present invention will be described in more detail with respect to such salts. These salts are well known and include ammonium, IPA, alkali metal (such as the mono-, di-, and trisodium salts, and the mono-, di-, and tripotassium salts), and trimethylsulfonium salts. Salts of N-phosphonomethylglycine are commercially significant in part because they are water soluble. The salts listed immediately above are highly water soluble, thereby allowing for highly concentrated solutions that can be diluted at the site of use. In accordance with the method of this invention as it pertains to glyphosate herbicide, an aqueous solution containing a herbicidally effective amount of glyphosate and other components in accordance with the invention is applied to foliage of plants. Such an aqueous solution can be obtained by dilution of a concentrated glyphosate salt solution with water, or dissolution or dispersion in water of a dry (e.g. granular, powder, tablet or briquette) glyphosate formulation.

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

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

The herbicidal effectiveness data set forth herein report "inhibition" as a percentage following a standard procedure in the art which reflects a visual assessment of plant mortality and growth reduction by comparison with untreated plants, made by technicians specially trained to make and record such observations. In all cases, a single technician makes all assessments of percent inhibition within any one experiment or trial. Such measurements are relied upon and regularly reported by Monsanto Company in the course of its herbicide business.

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

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

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

Annual broadleaves:

velvetleaf (*Abutilon theophrasti*)
5 pigweed (*Amaranthus* spp.)
buttonweed (*Borreria* spp.)
oilseed rape, canola, indian mustard, etc. (*Brassica* spp.)
commelina (*Commelina* spp.)
filaree (*Erodium* spp.)
10 sunflower (*Helianthus* spp.)
morningglory (*Ipomoea* spp.)
kochia (*Kochia scoparia*)
mallow (*Malva* spp.)
wild buckwheat, smartweed, etc. (*Polygonum* spp.)
15 purslane (*Portulaca* spp.)
russian thistle (*Salsola* spp.)
sida (*Sida* spp.)
wild mustard (*Sinapis arvensis*)
cocklebur (*Xanthium* spp.)

20 Annual narrowleaves:

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

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Perennial broadleaves:

mugwort (*Artemisia* spp.)milkweed (*Asclepias* spp.)canada thistle (*Cirsium arvense*)5 field bindweed (*Convolvulus arvensis*)kudzu (*Pueraria* spp.)

Perennial narrowleaves:

brachiaria (*Brachiaria* spp.)10 bermudagrass (*Cynodon dactylon*)yellow nutsedge (*Cyperus esculentus*)purple nutsedge (*C. rotundus*)quackgrass (*Elymus repens*)lalang (*Imperata cylindrica*)15 perennial ryegrass (*Lolium perenne*)guineagrass (*Panicum maximum*)dallisgrass (*Paspalum dilatatum*)reed (*Phragmites* spp.)johnsongrass (*Sorghum halepense*)20 cattail (*Typha* spp.)

Other perennials:

horsetail (*Equisetum* spp.)bracken (*Pteridium aquilinum*)25 blackberry (*Rubus* spp.)gorse (*Ulex europaeus*)

Thus, the method of the present invention, as it pertains to glyphosate herbicide, can be useful on any of the above species.

30 Effectiveness in greenhouse tests, usually at exogenous chemical rates lower than those normally effective in the field, is a proven indicator of consistency of field performance at normal use rates. However, even the most promising composition sometimes fails to exhibit enhanced performance in individual greenhouse tests. As illustrated in the Examples herein, a pattern of enhancement emerges over a series of greenhouse tests; when such a pattern is identified this is strong evidence of biological
35 enhancement that will be useful in the field.

Compositions of the present invention include one or more long-chain alkylether surfactants

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having the formula VI above. R^{12} can be branched or unbranched, saturated or unsaturated. R^{12} is preferably straight chain saturated C_{16} alkyl (cetyl) or straight chain saturated C_{18} alkyl (stearyl). In preferred alkylethers m is 0, n is an average number from about 20 to about 40 and R^{13} is preferably hydrogen. ~~Among especially preferred alkylether surfactants are those identified in the International~~
5 ~~Cosmetic Ingredient Directory as ceteth-20, cetareth-20, cetareth-27, steareth-20 and steareth-30.~~

Aqueous concentrate compositions in some circumstances are limited in the degree to which an exogenous chemical such as glyphosate can be loaded. At some point, as the loading of exogenous chemical is increased, the composition will not remain suitably stable. Addition of a small amount of colloidal particulate to such compositions has surprisingly been found to greatly increase loading ability
10 while retaining desired stability. Inclusion of such colloidal particulates can also enhance biological activity of an exogenous chemical formulation. Oxides of silicon, aluminum and titanium are preferred colloidal particulate materials. Particle size is preferably such that specific surface area is in the range from about 50 to about 400 m^2/g . Where the exogenous chemical is glyphosate, the use of colloidal particulate enables glyphosate acid equivalent loadings of at least 30% by weight for compositions
15 containing sufficient alkylether and fatty acid ester to show enhanced herbicidal effectiveness, or at least 40% by weight for compositions containing alkylether but no fatty acid ester, and showing herbicidal effectiveness at least equal to current commercial products loaded at about 30% by weight. We have found especially useful improvement in storage stability can be obtained using colloidal particulates having specific surface area between about 180 and about 400 m^2/g .

20 Other means of improving stability of highly loaded compositions may also be possible and are within the scope of the present invention.

Compositions in accordance with the present invention are typically prepared by combining water, the exogenous chemical, the alkylether surfactant, and other ingredients such as colloidal particulates and/or fatty acid esters if such ingredients are to be used. Details of specific processes used
25 to prepare such compositions are included in the Examples herein.

The concentrations of the various components will vary, in part depending on whether a concentrate is being prepared that will be further diluted before spraying onto a plant, or whether a solution or dispersion is being prepared that can be sprayed without further dilution.

In an aqueous glyphosate formulation that includes a C_{16-18} alkylether surfactant and butyl stearate, suitable concentrations can be: glyphosate 0.1 - 400 g a.e./l, alkylether surfactant 0.001 - 10%
30 by weight, and butyl stearate 0.001 - 10% by weight. To achieve the higher concentrations in these ranges, it is often beneficial to add other ingredients to provide acceptable storage stability, for example colloidal particulate silica or aluminum oxide at 0.5 - 2.5% by weight. In an aqueous glyphosate formulation that includes a C_{16-18} alkylether surfactant but no butyl stearate, glyphosate concentration
35 can suitably be increased to 500 g a.e./l or more, in the presence of a colloidal particulate at 0.5 - 2.5% by weight.

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In solid glyphosate formulations, higher concentrations of ingredients are possible because of the elimination of most of the water.

Although various compositions of the present invention are described herein as comprising certain listed materials, in some preferred embodiments of the invention the compositions consist essentially of the indicated materials.

Optionally, other agriculturally acceptable materials can be included in the compositions. For example, more than one exogenous chemical can be included. Also, various agriculturally acceptable adjuvants can be included, whether or not their purpose is to directly contribute to the effect of the exogenous chemical on a plant. For example, when the exogenous chemical is a herbicide, liquid nitrogen fertilizer or ammonium sulfate might be included in the composition. As another example, stabilizers can be added to the composition. In some instances it might be desirable to include microencapsulated acid in the composition, to lower the pH of a spray solution on contact with a leaf. One or more surfactants can also be included. Surfactants mentioned here by trade name, and other surfactants that can be useful in the method of the invention, are indexed in standard reference works such as McCutcheon's Emulsifiers and Detergents, 1997 edition, Handbook of Industrial Surfactants, 2nd Edition, 1997, published by Gower, and International Cosmetic Ingredient Dictionary, 6th Edition, 1995.

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

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

Many exogenous chemicals (including glyphosate herbicide) must be taken up by living tissues of the plant and translocated within the plant in order to produce the desired biological (e.g., herbicidal) effect. Thus, it is important that a herbicidal composition not be applied in such a manner as to excessively injure and interrupt the normal functioning of the local tissue of the plant so quickly that translocation is reduced. However, some limited degree of local injury can be insignificant, or even beneficial, in its impact on the biological effectiveness of certain exogenous chemicals.

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A large number of compositions of the invention are illustrated in the Examples that follow. Many concentrate compositions of glyphosate have provided sufficient herbicidal effectiveness in greenhouse tests to warrant field testing on a wide variety of weed species under a variety of application conditions. Aqueous compositions tested in the field comprising an alkylether surfactant and/or

5 containing a fatty acid ester have included:

Field composition	Glyphosate g a.e./l	% w/w		Type of surfactant	Type of fatty acid ester
		Fatty acid ester	Surfactant		
F-5	163	1.0	10.0	oleth-20	Bu stearate
F-8	163	1.0	10.0	steareth-20	Bu stearate
F-11	163	0.5	5.0	oleth-20	Bu stearate
F-12	163	0.3	5.0	oleth-20	Bu stearate
F-13	163	0.3	2.5	oleth-20	Bu stearate
F-16	163	0.5	5.0	steareth-20	Bu stearate
F-17	163	0.5	5.0	ceteth-20	Bu stearate
F-19	163	0.5	5.0	ceteareth-27	Bu stearate
F-22	163		5.0	steareth-20	
F-23	163		5.0	ceteth-20	
F-24	163		5.0	laureth-23	
F-25	163	0.3	5.0	ceteareth-27	Bu stearate
F-26	163	0.3	2.5	ceteareth-27	Bu stearate
F-27	163		5.0	ceteareth-27	
F-28	163	0.5	5.0	ceteareth-27	Me stearate
F-29	163	0.5	5.0	steareth-20	Me stearate
F-30	163	0.5	5.0	oleth-20	
F-33	163	0.5	5.0	ceteareth-15	Bu stearate
F-34	163		5.0	ceteareth-15	
F-35	163	0.5	5.0	steareth-30	Bu stearate

The above compositions were prepared by process (vii) if they contain fatty acid ester and by process (viii) if they do not. Both processes are described in the Examples.

Aqueous compositions tested in the field containing colloidal particulates have included:

Field composition	Glyphosate g a.e./l	% w/w				Type of surfactant	Type of colloidal particulate	Type of fatty acid ester	Other ingredients
		Fatty acid ester	Surf- actant	Coll. partic.	Other				
F-36	360	1.0	10.0	1.3		steareth-20	Aerosil 380	Bu stearate	
F-37	360	1.0	10.0	1.3		oleth-20	Aerosil 380	Bu stearate	
F-38	360	1.0	10.0	1.3		steareth-30	Aerosil 380	Bu stearate	
F-39	360		10.0	1.3		steareth-30	Aerosil 380		
F-50	360	1.0	10.0	1.3		ceteareth-15	Aerosil 380	Bu stearate	
F-51	360	1.0	10.0	1.3		ceteth-20	Aerosil 380	Bu stearate	
F-52	360	1.0	10.0	1.3		steareth-20	Aerosil 380	Bu stearate	
F-53	360	1.0	10.0	1.3		oleth-20	Aerosil 380	Bu stearate	
F-54	360	1.0	10.0	1.3		ceteareth-27	Aerosil 380	Bu stearate	
F-55	360	1.0	10.0	1.3		steareth-30	Aerosil 380	Bu stearate	

Field composition	Glyphosate g a.e./l	% w/w				Type of surfactant	Type of colloidal particulate	Type of fatty acid ester	Other ingredients
		Fatty acid ester	Surfactant	Coll. partic.	Other				
F-56	360		10.0	1.3		steareth-30	Aerosil 380		
F-57	360		10.0	1.3		cetareth-27	Aerosil 380		
F-58	360		10.0	1.3		steareth-20	Aerosil 380		
F-59	360		10.0	1.3		oleth-20	Aerosil 380		
F-60	360	1.0	10.0	1.3		cetareth-27	Aerosil 380	Me stearate	
F-61	360	1.0	10.0	1.3		cetareth-27	Aerosil 380	Me palmitate	
F-62	300		10.0	1.3		cetareth-27	Aerosil 380		
F-63	240		10.0	1.3		cetareth-27	Aerosil 380		
F-64	360		6.0	1.3		cetareth-27	Aerosil 380		
F-65	300		6.0	1.3		cetareth-27	Aerosil 380		
F-66	240		6.0	1.3		cetareth-27	Aerosil 380		
F-84	480		3.0	0.8		steareth-20	Aerosil 380		
F-85	480		3.0	1.5		oleth-20	Aerosil 380		
F-86	480		3.0	1.5		oleth-20	Aerosil MOX-170		
F-87	480		3.0	1.5		oleth-20	Aerosil OX-50		
F-89	480		3.0	1.5		steareth-20	Aerosil blend 2		
F-90	480		3.0	1.5		oleth-20	Aerosil blend 2		
F-91	480		4.5	1.5		oleth-20	Aerosil 380		
F-92	480		4.5	1.5		steareth-20	Aerosil 380		
F-93	480		3.0	1.5		steareth-20	Aerosil blend 1		
F-94	480		1.0	1.5		steareth-20	Aerosil blend 1		
F-95	480		6.0	1.5		steareth-20	Aerosil blend 1		
F-96	480		4.5	1.5	0.5	steareth-20	Aerosil blend 2		propylene glycol
F-97	480		6.0	1.5	0.5	steareth-20	Aerosil blend 2		propylene glycol
F-98	480		6.0	1.5	0.5	oleth-20	Aerosil blend 2		propylene glycol
F-99	480		4.5 + 2.3	1.5	0.5	steareth-20 + Ethomeen T/25	Aerosil blend 2		propylene glycol
F-100	480		6.0	1.5		steareth-20	Al oxide C		
F-101	480		4.5 + 2.3	1.5	0.5	steareth-20 + Ethomeen T/25	Al oxide C		propylene glycol
F-102	480		4.5 + 1.0	1.5	0.5	steareth-20 + Ethomeen T/25	Al oxide C		propylene glycol
F-103	480		3.0	1.5		steareth-20	Aerosil 380		
F-104	480		4.5	1.5		steareth-20	Al oxide C		
F-105	480		6.0	1.5		steareth-20	Aerosil 380		

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Field composition	Glyphosate g a.e./l	% w/w				Type of surfactant	Type of colloidal particulate	Type of fatty acid ester	Other ingredients
		Fatty acid ester	Surfactant	Coll. partic.	Other				
F-106	480		4.5 + 1.0	1.5	0.5	steareth-20 + Ethomeen T/25	Aerosil 380		propylene glycol
F-107	480		4.5 + 2.3	1.5	0.5	steareth-20 + Ethomeen T/25	Aerosil 380		propylene glycol
F-108	480		4.5	1.5		steareth-20	Aerosil blend 2		
F-109	480		6.0	1.5		steareth-20	Aerosil blend 2		
F-110	480		4.5 + 1.0	1.5	0.5	steareth-20 + Ethomeen T/25	Aerosil blend 2		propylene glycol
F-111	480		4.5	1.5		steareth-30	Aerosil blend 2		
F-112	480		4.5 + 1.0	1.5	0.5	steareth-20 + Ethomeen T/25	Aerosil blend 2		propylene glycol
F-113	480		6.0	1.5		steareth-30	Aerosil blend 2		
F-114	480		4.5 + 2.3	1.5	0.5	steareth-20 + Ethomeen T/25	Aerosil blend 2		propylene glycol
F-115	480		10.0	1.5		steareth-20	Aerosil blend 2		
F-116	480		4.5	1.5		cetareth-27	Aerosil 380		
F-117	480		6.0	1.5		cetareth-27	Aerosil 380		
F-118	480		4.5	1.5		cetareth-27	Aerosil blend 2		
F-119	480		6.0	1.5		cetareth-27	Aerosil blend 2		
F-120	480		4.5	1.5		cetareth-27	Al oxide C		
F-121	480		6.0	1.5		cetareth-27	Al oxide C		

Aerosil blend 1: Aerosil MOX-80 + Aerosil MOX-170 (1:1)

Aerosil blend 2: Aerosil MOX-80 + Aerosil 380 (1:2)

The above compositions were prepared by process (ix) as described in the Examples.

5 Aqueous compositions tested in the field comprising soybean lecithin (45% phospholipid, Avanti), alkylether surfactant and fatty acid ester have included:

Field composition	Glyphosate g a.e./l	% w/w				Type of surfactant	Type of fatty acid ester
		Lecithin	MON 0818	Fatty acid ester	Surfactant		
F-136	360	6.0	4.5	1.5	3.0 + 4.5	cetareth-27 + Ethomeen T/25	Bu stearate

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Field composition	Glyphosate g a.e./l	% w/w				Type of surfactant	Type of fatty acid ester
		Lecithin	MON 0818	Fatty acid ester	Surfactant		
F-138	228	0.8		3.8	3.0 + 3.0	cetareth-27 + Ethomeen T/25	Bu stearate
F-139	228	1.5		1.5	3.0 + 3.0	cetareth-27 + Ethomeen T/25	Bu stearate

The above compositions were prepared by process (x) as described in the Examples.

Dry compositions tested in the field have included:

Field composition	% w/w					Type of surfactant	Type of colloidal particulate	Other ingredients
	Glyphosate a.e.	Butyl stearate	Surfactant	Colloidal particulate	Other			
F-156	64		25.0	2.0		steareth-20	Aerosil blend 1	
F-157	68		20.0	2.0		steareth-20	Aerosil blend 1	
F-158	72		15.0	2.0		steareth-20	Aerosil blend 1	
F-159	64		25.0	1.0		ceteth-20	Aerosil 380	
F-160	65		25.0	1.0		steareth-20	Aerosil 380	
F-161	65		25.0	1.0		oleth-20	Aerosil 380	
F-166	68		20.0	2.0		steareth-20	Aerosil blend 1	
F-167	66	2.0	20.0	2.0		steareth-20	Aerosil blend 1	
F-168	68		20.0	2.0		oleth-20	Aerosil blend 1	
F-169	66	2.0	20.0	2.0		oleth-20	Aerosil blend 1	
F-170	66	2.0	20.0	2.0		cetareth-27	Aerosil blend 1	
F-171	48		14.1		36.1	cetareth-27		NH ₄ phosphate
F-172	65		20.0		5.0	cetareth-27		Na acetate
F-173	70		20.0			cetareth-27		

Aerosil blend 1: Aerosil MOX-80 + Aerosil MOX-170 (1:1)

The above compositions were prepared by the process described for dry granular compositions in Example 40.

EXAMPLES

In the following Examples illustrative of the invention, greenhouse tests were conducted to evaluate relative herbicidal effectiveness of glyphosate compositions. Compositions included for comparative purposes included the following:

Formulation B: which consists of 41% by weight of glyphosate IPA salt in aqueous solution. This formulation is sold in the USA by Monsanto Company under the ACCORD® trademark.

Formulation C: which consists of 41% by weight of glyphosate IPA salt in aqueous solution with a coformulant (15% by weight) of a surfactant (MON 0818 of Monsanto Company) based on polyoxyethylene (15) tallowamine. This formulation is sold in Canada by Monsanto Company under the ROUNDUP® trademark.

Formulation J: which consists of 41% by weight of glyphosate IPA salt in aqueous solution,

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that formulation. With some combinations of ingredients, a limit will be reached at which any further reduction of water content in the concentrate will cause it to become unstable (e.g., to separate into discrete layers), which may make it commercially unacceptable.

Accordingly, a need exists for improved formulations of exogenous chemicals, particularly herbicides, that are stable, effective, less sensitive to environmental conditions, and permit the use of reduced amounts of exogenous chemical to achieve the desired biological effect in or on plants. A need also exists for stable liquid concentrate formulations of exogenous chemicals that contain less water and more exogenous chemical than prior art concentrates.

SUMMARY OF THE INVENTION

The present invention relates to novel methods and compositions wherein exogenous chemicals are applied to plants to generate a desired biological response.

One embodiment of the present invention is a plant treatment composition that comprises (a) an exogenous chemical and (b) a first excipient substance which forms liposomes in aqueous dispersion and which consists of one or more compounds each having (i) a hydrophilic moiety comprising a cationic group and (ii) a hydrophobic moiety comprising two hydrocarbyl or acyl chains, wherein about 40 to 100 percent of said chains in the composition are saturated linear alkyl or acyl groups having about 8 to about 22 carbon atoms, preferably about 12 to about 18 carbon atoms. Preferably the cationic group is an amine or ammonium group. An "excipient substance" as that term is used in this patent is any substance other than the exogenous chemical and water that is added to the composition, and that satisfies the other conditions described. "Excipient substances" include inert ingredients, although an excipient substance useful in the present invention does not have to be devoid of biological activity.

In a preferred embodiment, the first excipient substance comprises one or more phospholipids selected from the group consisting of di-C₈₋₂₂-acylphosphatidylcholines and di-C₈₋₂₂-acylphosphatidylethanolamines, wherein about 40 to 100 percent of all acyl chains in said phospholipids are saturated alkanoyl chains. In a more specific embodiment, the first excipient substance is a phospholipid or mixture of phospholipids, about 40 to 100 percent of which consists of a dipalmitoyl or distearoyl ester of phosphatidylcholine or a mixture thereof. In one preferred embodiment, the weight/weight ratio of the first excipient substance to the exogenous chemical is about 1:3 to about 1:100.

A wide variety of exogenous chemicals can be used in the compositions and methods of the present invention. A preferred class is foliar-applied exogenous chemicals, i.e. exogenous chemicals that are normally applied post-emergence to foliage of plants. A preferred subclass of foliar-applied exogenous chemicals is those that are water-soluble. By "water-soluble" in this context is meant having a solubility in distilled water at 25°C greater than about 1% by weight. Especially preferred water-soluble exogenous chemicals are salts that have an anion portion and a cation portion. In one embodiment of the invention, at least one of the anion and cation portions is biologically active and has a

carbazone + MCPA, Tritosulfuron + Amicarbazone + Mecoprop-P, Tri-
 tosulfuron + Pethoxamid + Acifluorfen, Tritosulfuron + Pethoxamid
 + Azafenidin, Tritosulfuron + Pethoxamid + Benzfendizon, Trito-
 sulfuron + Pethoxamid + Butafenacil, Tritosulfuron + Pethoxamid +
 5 Cinidon-ethyl, Tritosulfuron + Pethoxamid + Flufenpyr, Tritosul-
 furon + Pethoxamid + Flufenpyr-ethyl, Tritosulfuron + Pethoxamid
 + Flumiclorac-pentyl, Tritosulfuron + Pethoxamid + Fluthiacet-
 methyl, Tritosulfuron + Pethoxamid + Oxyfluorfen, Tritosulfuron +
 Pethoxamid + Profluazol, Tritosulfuron + Pethoxamid + 2,4-D, Tri-
 10 tosulfuron + Pethoxamid + 2,4-DB, Tritosulfuron + Pethoxamid +
 Dicamba, Tritosulfuron + Pethoxamid + Dichlorprop-P, Tritosulfu-
 ron + Pethoxamid + Fluroxypyr, Tritosulfuron + Pethoxamid + Flu-
 roxypyr-meptyl, Tritosulfuron + Pethoxamid + MCPA, Tritosulfuron
 + Pethoxamid + Mecoprop-P, Tritosulfuron + Mesotrione + Acifluor-
 15 fen, Tritosulfuron + Mesotrione + Azafenidin, Tritosulfuron + Me-
 sotrione + Benzfendizon, Tritosulfuron + Mesotrione + Butafena-
 cil, Tritosulfuron + Mesotrione + Cinidon-ethyl, Tritosulfuron +
 Mesotrione + Flufenpyr, Tritosulfuron + Mesotrione + Flufenpyr-
 ethyl, Tritosulfuron + Mesotrione + Flumiclorac-pentyl, Tritosul-
 20 furon + Mesotrione + Fluthiacet-methyl, Tritosulfuron + Meso-
 trione + Oxyfluorfen, Tritosulfuron + Mesotrione + Profluazol,
 Tritosulfuron + Mesotrione + 2,4-D, Tritosulfuron + Mesotrione +
 2,4-DB, Tritosulfuron + Mesotrione + Dicamba, Tritosulfuron + Me-
 sotrione + Dichlorprop-P, Tritosulfuron + Mesotrione + Fluroxy-
 25 pyr, Tritosulfuron + Mesotrione + Fluroxypyr-meptyl, Tritosulfu-
 ron + Mesotrione + MCPA, Tritosulfuron + Mesotrione + Mecoprop-P,
 Tritosulfuron + Mesosulfuron-methyl + Acifluorfen, Tritosulfuron
 + Mesosulfuron-methyl + Azafenidin, Tritosulfuron + Mesosulfuron-
 methyl + Benzfendizon, Tritosulfuron + Mesosulfuron-methyl + Bu-
 30 tafenacil, Tritosulfuron + Mesosulfuron-methyl + Cinidon-ethyl,
 Tritosulfuron + Mesosulfuron-methyl + Flufenpyr, Tritosulfuron +
 Mesosulfuron-methyl + Flufenpyr-ethyl, Tritosulfuron + Mesosulfu-
 ron-methyl + Flumiclorac-pentyl, Tritosulfuron + Mesosulfuron-
 methyl + Fluthiacet-methyl, Tritosulfuron + Mesosulfuron-methyl +
 35 Oxyfluorfen, Tritosulfuron + Mesosulfuron-methyl + Profluazol,
 Tritosulfuron + Mesosulfuron-methyl + 2,4-D, Tritosulfuron + Me-
 sosulfuron-methyl + 2,4-DB, Tritosulfuron + Mesosulfuron-methyl +
 Dicamba, Tritosulfuron + Mesosulfuron-methyl + Dichlorprop-P,
 Tritosulfuron + Mesosulfuron-methyl + Fluroxypyr, Tritosulfuron +
 40 Mesosulfuron-methyl + Fluroxypyr-meptyl, Tritosulfuron + Mesosul-
 furon-methyl + MCPA, Tritosulfuron + Mesosulfuron-methyl + Meco-
 prop-P, Tritosulfuron + Mesosulfuron-methyl + Mefenpyr-diethyl +
 Acifluorfen, Tritosulfuron + Mesosulfuron-methyl + Mefenpyr-
 diethyl + Azafenidin, Tritosulfuron + Mesosulfuron-methyl + Me-
 45 fenpyr-diethyl + Benzfendizon, Tritosulfuron + Mesosulfuron-
 methyl + Mefenpyr-diethyl + Butafenacil; Tritosulfuron + Mesosul-
 furon-methyl + Mefenpyr-diethyl + Cinidon-ethyl, Tritosulfuron +

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molecular weight of less than about 300. Particular examples of such exogenous chemicals where the cation portion is biologically active are paraquat, diquat and chlormequat. More commonly it is the anion portion that is biologically active.

Another preferred subclass of exogenous chemicals is those that exhibit systemic biological activity in the plant. Within this subclass, an especially preferred group of exogenous chemicals is N-phosphonomethylglycine and its herbicidal derivatives. N-phosphonomethylglycine, often referred to by its common name glyphosate, can be used in its acid form, but is more preferably used in the form of a salt. Any water-soluble salt of glyphosate can be used in the practice of this invention. Some preferred salts include the sodium, potassium, ammonium, mono-, di-, tri- and tetra-C₁₋₄-alkylammonium, mono-, di- and tri-C₁₋₄-alkanolammonium, mono-, di- and tri-C₁₋₄-alkylsulfonium and sulfoxonium salts. The ammonium, monoisopropylammonium and trimethylsulfonium salts of glyphosate are especially preferred. Mixtures of salts can also be useful in certain situations.

A composition of the present invention comprising an exogenous chemical and a first excipient substance as described above can have a number of different physical forms. For example, the composition can further comprise water in an amount effective to make the composition a dilute aqueous composition ready for application to foliage of a plant. Such a composition typically contains about 0.02 to about 2 percent by weight of the exogenous chemical, but for some purposes can contain up to about 10 percent by weight or even more of the exogenous chemical.

Alternatively, the composition can be a shelf-stable concentrate composition comprising the exogenous chemical substance in an amount of about 10 to about 90 percent by weight. Such shelf-stable concentrates can be, for example, (1) a solid composition comprising the exogenous chemical substance in an amount of about 30 to about 90 percent by weight, such as a water-soluble or water-dispersible granular formulation, or (2) a composition that further comprises a liquid diluent, wherein the composition comprises the exogenous chemical substance in an amount of about 10 to about 60 percent by weight. In this latter embodiment, it is especially preferred for the exogenous chemical substance to be water-soluble and present in an aqueous phase of the composition in an amount of about 15 to about 45 percent by weight of the composition. In particular, such a composition can be, for example, an aqueous solution concentrate or an emulsion having an oil phase. If it is an emulsion, it can more specifically be, for example, an oil-in-water emulsion, a water-in-oil emulsion, or a water-in-oil-in-water multiple emulsion.

As described above, one embodiment of the invention is a sprayable composition. The term "spray composition" is sometimes used herein to mean a sprayable composition.

In a related embodiment of the invention, a concentrate composition is provided which, upon dilution, dispersion or dissolution in water forms the sprayable composition just described. The concentrate composition contains a reduced amount of the aqueous diluent, or, in a particular embodiment, is a dry composition having less than about 5% water by weight. Typically a concentrate

furon-methyl + Dicamba, Tritosulfuron + Iodosulfuron-methyl + Dichlorprop-P, Tritosulfuron + Iodosulfuron-methyl + Fluroxypyr, Tritosulfuron + Iodosulfuron-methyl + Fluroxypyr-meptyl, Tritosulfuron + Iodosulfuron-methyl + MCPA, Tritosulfuron + Iodosulfuron-methyl + Mecoprop-P, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Acifluorfen, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Azafenidin, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Benzfendizon, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Butafenacil, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Cinidon-ethyl, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Flufenpyr, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Flufenpyr-ethyl, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Flumiclorac-pentyl, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Fluthiacet-methyl, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Oxyfluorfen, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Profluazol, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + 2,4-D, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + 2,4-DB, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Dicamba, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Dichlorprop-P, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Fluroxypyr, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Fluroxypyr-meptyl, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + MCPA, Tritosulfuron + Iodosulfuron-methyl + Mefenpyr-diethyl + Mecoprop-P, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Acifluorfen, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Azafenidin, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Benzfendizon, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Butafenacil, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Cinidon-ethyl, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Flufenpyr, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Flufenpyr-ethyl, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Flumiclorac-pentyl, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Fluthiacet-methyl, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Oxyfluorfen, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Profluazol, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + 2,4-D, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + 2,4-DB, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Dicamba, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Dichlorprop-P, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Fluroxypyr, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Fluroxypyr-meptyl, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + MCPA, Tritosulfuron + Iodosulfuron-methyl + Isoxadifen-ethyl + Mecoprop-P, Tritosulfuron + Foramsulfuron +

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composition of the invention contains at least about 10% by weight of the exogenous chemical, preferably at least about 15%.

The weight ratio of the first excipient substance to the exogenous chemical preferably is between about 1:3 and about 1:100. We have been surprised by the high level of biological effectiveness, specifically herbicidal effectiveness of a glyphosate composition, exhibited at such low ratios of first excipient substance to exogenous chemical. Higher ratios can also be effective but are likely to be uneconomic in most situations and increase the risk of producing an antagonistic effect on effectiveness of the exogenous chemical.

Prior art exogenous chemical compositions that have included liposome-forming excipient substances have typically contained a higher percentage of the liposome-forming excipient substance than of the exogenous chemical. Compositions of the present invention can contain less of the excipient substance than the exogenous chemical, and in some embodiments much less. This makes such compositions of the present invention much less expensive than the above-described prior art compositions. It is surprising that the enhancement of biological activity that has been observed when using the present invention can be achieved with the addition of relatively small amounts of such excipient substances.

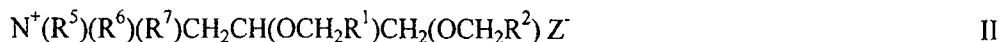
As indicated above, the first excipient substance comprises a liposome-forming compound having a hydrophilic moiety that comprises a cationic group and a hydrophobic moiety that comprises two independently saturated or unsaturated hydrocarbyl or acyl chains. Liposome-forming compounds useful in the invention can illustratively be represented as in formulas I-IV below. All such compounds have two hydrocarbyl chains R^1 and R^2 each independently having about 7 to about 21 carbon atoms. A number of subclasses of such liposome-forming compounds are known.

One subclass has the formula



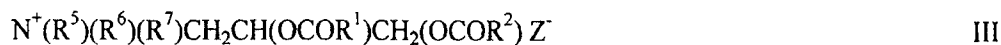
wherein R^3 and R^4 are independently hydrogen, C_{1-4} alkyl or C_{1-4} hydroxyalkyl and Z is a suitable agriculturally acceptable anion.

A second subclass has the formula



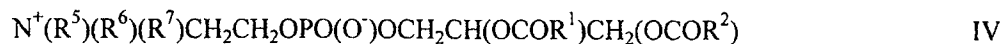
wherein R^5 , R^6 and R^7 are independently hydrogen, C_{1-4} alkyl or C_{1-4} hydroxyalkyl and Z is a suitable anion.

A third subclass has the formula



wherein R^5 , R^6 , R^7 and Z are as defined above.

A fourth subclass has the formula



wherein R^5 , R^6 , and R^7 are as defined above.

Mesosulfuron-methyl + Mefenpyr-diethyl + Flufenpyr, Tritosulfuron
 + Mesosulfuron-methyl + Mefenpyr-diethyl + Flufenpyr-ethyl, Tri-
 to sulfuron + Mesosulfuron-methyl + Mefenpyr-diethyl + Flumiclo-
 rac-pentyl, Tritosulfuron + Mesosulfuron-methyl + Mefenpyr-
 5 diethyl + Fluthiacet-methyl, Tritosulfuron + Mesosulfuron-methyl
 + Mefenpyr-diethyl + Oxyfluorfen, Tritosulfuron + Mesosulfuron-
 methyl + Mefenpyr-diethyl + Profluazol, Tritosulfuron + Mesosul-
 furon-methyl + Mefenpyr-diethyl + 2,4-D, Tritosulfuron + Mesosul-
 furon-methyl + Mefenpyr-diethyl + 2,4-DB, Tritosulfuron + Meso-
 10 sulfuron-methyl + Mefenpyr-diethyl + Dicamba, Tritosulfuron + Me-
 sosulfuron-methyl + Mefenpyr-diethyl + Dichlorprop-P, Tritosulfu-
 ron + Mesosulfuron-methyl + Mefenpyr-diethyl + Fluroxypyr, Trito-
 sulfuron + Mesosulfuron-methyl + Mefenpyr-diethyl + Fluroxypyr-
 meptyl, Tritosulfuron + Mesosulfuron-methyl + Mefenpyr-diethyl +
 15 MCPA, Tritosulfuron + Mesosulfuron-methyl + Mefenpyr-diethyl +
 Mecoprop-P, Tritosulfuron + Mesosulfuron-methyl + Isoxadifen-
 ethyl + Acifluorfen, Tritosulfuron + Mesosulfuron-methyl + Isoxa-
 difen-ethyl + Azafenidin, Tritosulfuron + Mesosulfuron-methyl +
 Isoxadifen-ethyl + Benzfendizon, Tritosulfuron + Mesosulfuron-
 20 methyl + Isoxadifen-ethyl + Butafenacil, Tritosulfuron + Mesosul-
 furon-methyl + Isoxadifen-ethyl + Cinidon-ethyl, Tritosulfuron +
 Mesosulfuron-methyl + Isoxadifen-ethyl + Flufenpyr, Tritosulfuron
 + Mesosulfuron-methyl + Isoxadifen-ethyl + Flufenpyr-ethyl, Tri-
 to sulfuron + Mesosulfuron-methyl + Isoxadifen-ethyl + Flumiclo-
 25 rac-pentyl, Tritosulfuron + Mesosulfuron-methyl + Isoxadifen-
 ethyl + Fluthiacet-methyl, Tritosulfuron + Mesosulfuron-methyl +
 Isoxadifen-ethyl + Oxyfluorfen, Tritosulfuron + Mesosulfuron-
 methyl + Isoxadifen-ethyl + Profluazol, Tritosulfuron + Mesosul-
 furon-methyl + Isoxadifen-ethyl + 2,4-D, Tritosulfuron + Mesosul-
 30 furon-methyl + Isoxadifen-ethyl + 2,4-DB, Tritosulfuron + Meso-
 sulfuron-methyl + Isoxadifen-ethyl + Dicamba, Tritosulfuron + Me-
 sosulfuron-methyl + Isoxadifen-ethyl + Dichlorprop-P, Tritosulfu-
 ron + Mesosulfuron-methyl + Isoxadifen-ethyl + Fluroxypyr, Trito-
 sulfuron + Mesosulfuron-methyl + Isoxadifen-ethyl + Fluroxypyr-
 35 meptyl, Tritosulfuron + Mesosulfuron-methyl + Isoxadifen-ethyl +
 MCPA, Tritosulfuron + Mesosulfuron-methyl + Isoxadifen-ethyl +
 Mecoprop-P, Tritosulfuron + Iodosulfuron-methyl + Acifluorfen,
 Tritosulfuron + Iodosulfuron-methyl + Azafenidin, Tritosulfuron +
 Iodosulfuron-methyl + Benzfendizon, Tritosulfuron + Iodosulfuron-
 40 methyl + Butafenacil, Tritosulfuron + Iodosulfuron-methyl + Cini-
 don-ethyl, Tritosulfuron + Iodosulfuron-methyl + Flufenpyr, Tri-
 to sulfuron + Iodosulfuron-methyl + Flufenpyr-ethyl, Tritosulfuron
 + Iodosulfuron-methyl + Flumiclorac-pentyl, Tritosulfuron + Iodo-
 sulfuron-methyl + Fluthiacet-methyl, Tritosulfuron + Iodosulfu-
 45 ron-methyl + Oxyfluorfen, Tritosulfuron + Iodosulfuron-methyl +
 Profluazol, Tritosulfuron + Iodosulfuron-methyl + 2,4-D, Trito-
 sulfuron + Iodosulfuron-methyl + 2,4-DB, Tritosulfuron + Iodosul-

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Compounds of formulas I-IV will have the indicated formulas in an acid medium, for example at a pH of 4 and may have the same formulas at other pH's as well. It should be understood, however, that compositions of the present invention are not limited to use at a pH of 4.

It is preferred that about 40 to 100 percent of the R¹ and R² chains in the composition are saturated straight-chain alkyl groups each having about 7 to about 21 carbon atoms. Examples of suitable agriculturally acceptable anions Z include hydroxide, chloride, bromide, iodide, sulfate, phosphate and acetate.

In all of the above subclasses of liposome-forming substances, the hydrophilic moiety comprises a cationic group, specifically an amine or ammonium group. The compound as a whole is in some cases cationic (as in I, II and III) and in some cases neutral (as in IV). Where the amine group is quaternary, it behaves as a cationic group independently of pH. Where the amine group is secondary or tertiary, it behaves as a cationic group when protonated, i.e. in an acid medium, for example at a pH of 4.

In a preferred embodiment, the composition further comprises a second excipient substance that is an amphiphilic quaternary ammonium compound or mixture of such compounds. The hydrophobic moiety of the quaternary ammonium compound is a saturated alkyl or haloalkyl group having about 6 to about 22 carbon atoms.

Preferred quaternary ammonium compounds (other than those which are liposome-forming and have two hydrocarbyl chains) for use as the second excipient substance in compositions of the invention have the formula



wherein R⁸ represents the hydrophobic moiety and is a hydrocarbyl or haloalkyl group having from about 6 to about 22 carbon atoms, W and Y are independently O or NH, a and b are independently 0 or 1 but at least one of a and b is 1, X is CO, SO or SO₂, n is 2 to 4, R⁹, R¹⁰ and R¹¹ are independently C₁₋₄ alkyl, and T is a suitable anion. R⁸ in one particular embodiment is hydrocarbyl having about 12 to about 18 carbon atoms. R⁸ can also be fluorinated. In one specific embodiment, R⁸ is perfluorinated, and preferably has about 6 to about 12 carbon atoms. Suitable agriculturally acceptable anions T include hydroxide, chloride, bromide, iodide, sulfate, phosphate and acetate. In one particularly preferred embodiment, R⁸ is saturated perfluoroalkyl having about 6 to about 12 carbon atoms, X is CO or SO₂, Y is NH, a is 0, b is 1, n is 3, R⁹, R¹⁰ and R¹¹ are methyl, and T is selected from the group consisting of chloride, bromide and iodide.

In another preferred embodiment, the composition further comprises a second excipient substance which is a compound or mixture of compounds of formula



wherein R¹⁴ is a hydrocarbyl group having about 5 to about 21 carbon atoms, R¹⁵ is a hydrocarbyl group having 1 to about 14 carbon atoms, the total number of carbon atoms in R¹⁴ and R¹⁵ is about 11 to about 27, and A is O or NH.

- Acifluorfen, Tritosulfuron + Foramsulfuron + Azafenidin, Tritosulfuron + Foramsulfuron + Benzfendizon, Tritosulfuron + Foramsulfuron + Butafenacil, Tritosulfuron + Foramsulfuron + Cinidon-ethyl, Tritosulfuron + Foramsulfuron + Flufenpyr, Tritosulfuron +
- 5 Foramsulfuron + Flufenpyr-ethyl, Tritosulfuron + Foramsulfuron + Flumiclorac-pentyl, Tritosulfuron + Foramsulfuron + Fluthiacet-methyl, Tritosulfuron + Foramsulfuron + Oxyfluorfen, Tritosulfuron + Foramsulfuron + Profluazol, Tritosulfuron + Foramsulfuron + 2,4-D, Tritosulfuron + Foramsulfuron + 2,4-DB, Tritosulfuron +
- 10 Foramsulfuron + Dicamba, Tritosulfuron + Foramsulfuron + Dichlorprop-P, Tritosulfuron + Foramsulfuron + Fluroxypyr, Tritosulfuron + Foramsulfuron + Fluroxypyr-meptyl, Tritosulfuron + Foramsulfuron + MCPA, Tritosulfuron + Foramsulfuron + Mecoprop-P, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Acifluorfen, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Azafenidin, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Benzfendizon, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Butafenacil, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Cinidon-ethyl, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Flufenpyr, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Flufenpyr-ethyl, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Flumiclorac-pentyl, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Fluthiacet-methyl, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Oxyfluorfen, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl +
- 25 Profluazol, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + 2,4-D, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + 2,4-DB, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Dicamba, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Dichlorprop-P, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Fluroxypyr,
- 30 Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Fluroxypyr-meptyl, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + MCPA, Tritosulfuron + Foramsulfuron + Mefenpyr-diethyl + Mecoprop-P, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Acifluorfen, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Azafenidin,
- 35 Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Benzfendizon, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Butafenacil, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Cinidon-ethyl, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Flufenpyr, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Flufenpyr-
- 40 ethyl, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Flumiclorac-pentyl, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Fluthiacet-methyl, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Oxyfluorfen, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Profluazol, Tritosulfuron + Foramsulfuron + Isoxadifen-
- 45 ethyl + 2,4-D, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + 2,4-DB, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Dicamba, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Dich-

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R¹⁴ preferably has about 11 to about 21 carbon atoms, R¹⁵ preferably has 1 to about 6 carbon atoms and A is preferably O. In another, the second excipient substance is a C₁₋₄ alkyl ester of a C₁₂₋₁₈ fatty acid, for example a propyl, isopropyl or butyl ester of a C₁₂₋₁₈ fatty acid. Butyl stearate is an especially preferred example. The aqueous composition in embodiments comprising a compound of formula VII can be an emulsion comprising an oil phase that comprises said second excipient substance, for example a water-in-oil-in-water multiple emulsion or an oil-in-water emulsion.

In any of the above particular embodiments, the exogenous chemical and/or second excipient substance can be encapsulated within or associated with the liposomes formed by the first excipient substance, but do not necessarily have to be so encapsulated or associated. "Associated" in this context means bound to or at least partly intercalated in some fashion in a vesicle wall, as opposed to being encapsulated. In yet another embodiment of the invention, the exogenous chemical and/or second excipient substance is not encapsulated in or associated with the liposomes at all. Although the present invention does not exclude the possibility of so encapsulating or associating the exogenous chemical, a presently preferred dilute sprayable liposomal composition encapsulates less than 5% by weight of the exogenous chemical that is present in the overall composition. Another dilute sprayable liposomal embodiment of the present invention has no substantial amount (i.e., less than 1% by weight) of the exogenous chemical encapsulated in the liposomes. As a droplet of such a liposomal composition dries on foliage of a plant, the proportion of the exogenous chemical that is encapsulated in the liposomes may change. Compositions of the present invention that include an exogenous chemical can be applied to foliage of plants in an amount that is effective to achieve the desired biological effect of the exogenous chemical. For example, when the exogenous chemical is a postemergent herbicide, the composition can be applied to a plant in a herbicidally effective amount.

The compositions and methods of the present invention have a number of advantages. They provide enhanced biological activity of exogenous chemicals in or on plants in comparison with prior formulations, either in terms of greater ultimate biological effect, or obtaining an equivalent biological effect while using a reduced application rate of exogenous chemical. Certain herbicide formulations of the present invention can avoid antagonism that has been observed in some prior art herbicide formulations, and can minimize quick production of necrotic lesions on leaves that in some situations hinder overall translocation of herbicide in the plant. Certain herbicide compositions of the invention modify the spectrum of activity of the herbicide across a range of plant species. For example, certain formulations of the present invention containing glyphosate can provide good herbicidal activity against broadleaf weeds while not losing any herbicidal effectiveness on narrowleaf weeds. Others can enhance herbicidal effectiveness on narrowleaf weeds to a greater extent than on broadleaf weeds. Still others can have enhanced effectiveness which is specific to a narrow range of species or even a single species.

Another advantage of the present invention is that it generally employs relatively small amounts of the excipient substances in relation to the amount of exogenous chemical employed. This makes the

- lorprop-P, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Fluroxypyr, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + Fluroxypyr-meptyl, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl + MCPA, Tritosulfuron + Foramsulfuron + Isoxadifen-ethyl +
- 5 Mecoprop-P, Tritosulfuron + Flupyr-sulfuron-methyl + Acifluorfen, Tritosulfuron + Flupyr-sulfuron-methyl + Azafenidin, Tritosulfuron + Flupyr-sulfuron-methyl + Benzfendizon, Tritosulfuron + Flupyr-sulfuron-methyl + Butafenacil, Tritosulfuron + Flupyr-sulfuron-methyl + Cinidon-ethyl, Tritosulfuron + Flupyr-sulfuron-methyl +
- 10 Flufenpyr, Tritosulfuron + Flupyr-sulfuron-methyl + Flufenpyr-ethyl, Tritosulfuron + Flupyr-sulfuron-methyl + Flumiclorac-pentyl, Tritosulfuron + Flupyr-sulfuron-methyl + Fluthiacet-methyl, Tritosulfuron + Flupyr-sulfuron-methyl + Oxyfluorfen, Tritosulfuron + Flupyr-sulfuron-methyl + Profluazol, Tritosulfuron +
- 15 Flupyr-sulfuron-methyl + 2,4-D, Tritosulfuron + Flupyr-sulfuron-methyl + 2,4-DB, Tritosulfuron + Flupyr-sulfuron-methyl + Dicamba, Tritosulfuron + Flupyr-sulfuron-methyl + Dichlorprop-P, Tritosulfuron + Flupyr-sulfuron-methyl + Fluroxypyr, Tritosulfuron + Flupyr-sulfuron-methyl + Fluroxypyr-meptyl, Tritosulfuron + Flupyr-sulfuron-methyl + MCPA, Tritosulfuron + Flupyr-sulfuron-methyl +
- 20 Mecoprop-P, Tritosulfuron + Be-flubutamid + Acifluorfen, Tritosulfuron + Be-flubutamid + Azafenidin, Tritosulfuron + Be-flubutamid + Benzfendizon, Tritosulfuron + Be-flubutamid + Butafenacil, Tritosulfuron + Be-flubutamid + Cinidon-ethyl, Tritosulfuron + Be-flubu-
- 25 tamid + Flufenpyr, Tritosulfuron + Be-flubutamid + Flufenpyr-ethyl, Tritosulfuron + Be-flubutamid + Flumiclorac-pentyl, Tritosulfuron + Be-flubutamid + Fluthiacet-methyl, Tritosulfuron + Be-flubutamid + Oxyfluorfen, Tritosulfuron + Be-flubutamid + Profluazol, Tritosulfuron + Be-flubutamid + 2,4-D, Tritosulfuron + Be-flu-
- 30 butamid + 2,4-DB, Tritosulfuron + Be-flubutamid + Dicamba, Tritosulfuron + Be-flubutamid + Dichlorprop-P, Tritosulfuron + Be-flubutamid + Fluroxypyr, Tritosulfuron + Be-flubutamid + Fluroxypyr-meptyl, Tritosulfuron + Be-flubutamid + MCPA, Tritosulfuron + Be-flubutamid + Mecoprop-P, Tritosulfuron + Carfentrazon-ethyl +
- 35 Acifluorfen, Tritosulfuron + Carfentrazon-ethyl + Azafenidin, Tritosulfuron + Carfentrazon-ethyl + Benzfendizon, Tritosulfuron + Carfentrazon-ethyl + Butafenacil, Tritosulfuron + Carfentrazon-ethyl + Cinidon-ethyl, Tritosulfuron + Carfentrazon-ethyl + Flufenpyr, Tritosulfuron + Carfentrazon-ethyl + Flufenpyr-ethyl,
- 40 Tritosulfuron + Carfentrazon-ethyl + Flumiclorac-pentyl, Tritosulfuron + Carfentrazon-ethyl + Fluthiacet-methyl, Tritosulfuron + Carfentrazon-ethyl + Oxyfluorfen, Tritosulfuron + Carfentrazon-ethyl + Profluazol, Tritosulfuron + Carfentrazon-ethyl + 2,4-D, Tritosulfuron + Carfentrazon-ethyl + 2,4-DB, Tritosulfuron + Car-
- 45 fentrazon-ethyl + Dicamba, Tritosulfuron + Carfentrazon-ethyl + Dichlorprop-P, Tritosulfuron + Carfentrazon-ethyl + Fluroxypyr, Tritosulfuron + Carfentrazon-ethyl + Fluroxypyr-meptyl, Tritosul-

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compositions and methods of the present invention relatively inexpensive, and also tends to reduce instability problems in specific compositions where one or both excipient substances are physically incompatible with the exogenous chemical.

Further, compositions of the present invention are less sensitive in some instances to environmental conditions such as relative humidity at the time of application to the plant. Also, the present invention allows the use of smaller amounts of herbicides or other pesticides, while still obtaining the required degree of control of weeds or other undesired organisms.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

Examples of exogenous chemical substances that can be included in compositions of the present invention include, but are not limited to, chemical pesticides (such as herbicides, algicides, fungicides, bactericides, viricides, insecticides, aphicides, miticides, nematocides, molluscicides and the like), plant growth regulators, fertilizers and nutrients, gametocides, defoliants, desiccants, mixtures thereof and the like. In one embodiment of the invention, the exogenous chemical is polar.

A preferred group of exogenous chemicals are those that are normally applied post-emergence to the foliage of plants, i.e. foliar-applied exogenous chemicals.

Some exogenous chemicals useful in the present invention are water-soluble, for example salts that comprise biologically active ions, and also comprise counterions, which may be biologically inert or relatively inactive. A particularly preferred group of these water-soluble exogenous chemicals or their biologically active ions or moieties are systemic in plants, that is, they are to some extent translocated from the point of entry in the foliage to other parts of the plant where they can exert their desired biological effect. Especially preferred among these are herbicides, plant growth regulators and nematocides, particularly those that have a molecular weight, excluding counterions, of less than about 300. More especially preferred among these are exogenous chemical compounds having one or more functional groups selected from amine, carboxylate, phosphonate and phosphinate groups.

Among such compounds, an even more preferred group are herbicidal or plant growth regulating exogenous chemical compounds having at least one of each of amine, carboxylate, and either phosphonate or phosphinate functional groups. Salts of N-phosphonomethylglycine are examples of this group of exogenous chemicals. Further examples include salts of glufosinate, for instance the ammonium salt (ammonium DL-homoalanin-4-yl (methyl) phosphinate).

Another preferred group of exogenous chemicals which can be applied by the method of the invention are nematocides such as those disclosed in U.S. Patent No. 5,389,680, the disclosure of which is incorporated herein by reference. Preferred nematocides of this group are salts of 3,4,4-trifluoro-3-butenic acid or of N-(3,4,4-trifluoro-1-oxo-3-butenyl)glycine.

Exogenous chemicals which can usefully be applied by the method of the present invention are normally, but not exclusively, those which are expected to have a beneficial effect on the overall growth or yield of desired plants such as crops, or a deleterious or lethal effect on the growth of undesirable

- furon + Carfentrazon-ethyl + MCPA, Tritosulfuron + Carfentrazon-ethyl + Mecoprop-P, Tritosulfuron + Fluazolat + Acifluorfen, Tritosulfuron + Fluazolat + Azafenidin, Tritosulfuron + Fluazolat + Benzfendizon, Tritosulfuron + Fluazolat + Butafenacil, Tritosulfuron + Fluazolat + Cinidon-ethyl, Tritosulfuron + Fluazolat + Flufenpyr, Tritosulfuron + Fluazolat + Flufenpyr-ethyl, Tritosulfuron + Fluazolat + Flumiclorac-pentyl, Tritosulfuron + Fluazolat + Fluthiacet-methyl, Tritosulfuron + Fluazolat + Oxyfluorfen, Tritosulfuron + Fluazolat + Profluazol, Tritosulfuron + Fluazolat + 2,4-D, Tritosulfuron + Fluazolat + 2,4-DB, Tritosulfuron + Fluazolat + Dicamba, Tritosulfuron + Fluazolat + Dichlorprop-P, Tritosulfuron + Fluazolat + Fluroxypyr, Tritosulfuron + Fluazolat + Fluroxypyr-meptyl, Tritosulfuron + Fluazolat + MCPA, Tritosulfuron + Fluazolat + Mecoprop-P, Tritosulfuron + Pyraflufen-ethyl + Acifluorfen, Tritosulfuron + Pyraflufen-ethyl + Azafenidin, Tritosulfuron + Pyraflufen-ethyl + Benzfendizon, Tritosulfuron + Pyraflufen-ethyl + Butafenacil, Tritosulfuron + Pyraflufen-ethyl + Cinidon-ethyl, Tritosulfuron + Pyraflufen-ethyl + Flufenpyr, Tritosulfuron + Pyraflufen-ethyl + Flufenpyr-ethyl, Tritosulfuron + Pyraflufen-ethyl + Flumiclorac-pentyl, Tritosulfuron + Pyraflufen-ethyl + Fluthiacet-methyl, Tritosulfuron + Pyraflufen-ethyl + Oxyfluorfen, Tritosulfuron + Pyraflufen-ethyl + Profluazol, Tritosulfuron + Pyraflufen-ethyl + 2,4-D, Tritosulfuron + Pyraflufen-ethyl + 2,4-DB, Tritosulfuron + Pyraflufen-ethyl + Dicamba, Tritosulfuron + Pyraflufen-ethyl + Dichlorprop-P, Tritosulfuron + Pyraflufen-ethyl + Fluroxypyr, Tritosulfuron + Pyraflufen-ethyl + Fluroxypyr-meptyl, Tritosulfuron + Pyraflufen-ethyl + MCPA, Tritosulfuron + Pyraflufen-ethyl + Mecoprop-P.
- 30 Als herbizide Mischungen besonders bevorzugt sind die nachfolgend genannten Mischungen; soweit die Wirkstoffe Tritosulfuron, Flucarbazon, Propoxycarbazon, Dicamba, Mesosulfuron-methyl, Iodosulfuron-methyl, Foramsulfuron und/oder Flupyrsulfuron-methyl Bestandteile der Mischungen sind, sind außerdem auch diejenigen Mischungen bevorzugt, bei denen die genannten Wirkstoffe durch ihre Natrium-, Kalium- oder Calciumsalze ersetzt sind; des weiteren, soweit Dicamba Bestandteil der Mischungen ist, sind außerdem auch diejenigen Mischungen bevorzugt, bei denen Dicamba durch sein Ethanolammonium-, Diethanolammonium-, Methanolammonium-, Dimethanolammonium-, Trimethanolammonium-, Isopropylammonium- oder 2-(2-Hydroxyethoxy)ethylammonium-Salz ersetzt ist:

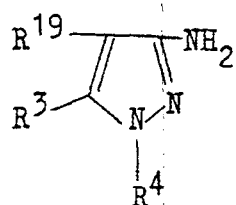
- Tritosulfuron + Flucarbazon, Tritosulfuron + Flucarbazon + Dicamba, Tritosulfuron + Propoxycarbazon, Tritosulfuron + Propoxycarbazon + Cinidon-ethyl, Tritosulfuron + Propoxycarbazon + Dicamba, Tritosulfuron + Mesosulfuron-methyl, Tritosulfuron + Mesosulfuron-methyl + Dicamba, Tritosulfuron + Mesosulfuron-methyl +

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plants such as weeds. The method of the present invention is particularly useful for herbicides, especially those that are normally applied post-emergence to the foliage of unwanted vegetation.

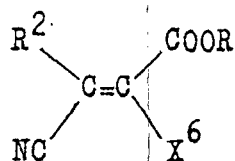
Herbicides which can be applied by the method of the present invention include but are not limited to any listed in standard reference works such as the "Herbicide Handbook," Weed Science Society of America, 1994, 7th Edition, or the "Farm Chemicals Handbook," Meister Publishing Company, 1997 Edition. Illustratively these herbicides include acetanilides such as acetochlor, alachlor and metolachlor, aminotriazole, asulam, bentazon, bialaphos, bipyridyls such as paraquat, bromacil, cyclohexenones such as clethodim and sethoxydim, dicamba, diflufenican, dinitroanilines such as pendimethalin, diphenylethers such as acifluorfen, fomesafen and oxyfluorfen, fatty acids such as C₉₋₁₀ fatty acids, fosamine, flupoxam, glufosinate, glyphosate, hydroxybenzonitriles such as bromoxynil, imidazolinones such as imazaquin and imazethapyr, isoxaben, norflurazon, phenoxyes such as 2,4-D, phenoxypropionates such as diclofop, fluazifop and quizalofop, picloram, propanil, substituted ureas such as fluometuron and isoproturon, sulfonyleureas such as chlorimuron, chlorsulfuron, halosulfuron, metsulfuron, primisulfuron, sulfometuron and sulfosulfuron, thiocarbamates such as triallate, triazines such as atrazine and metribuzin, and triclopyr. Herbicidally active derivatives of any known herbicide are also within the scope of the present invention. A herbicidally active derivative is any compound which is a minor structural modification, most commonly but not restrictively a salt or ester, of a known herbicide. These compounds retain the essential activity of the parent herbicide, but may not necessarily have a potency equal to that of the parent herbicide. These compounds may convert to the parent herbicide before or after they enter the treated plant. Mixtures or coformulations of a herbicide with other ingredients, or of more than one herbicide, may likewise be employed.

An especially preferred herbicide is N-phosphonomethylglycine (glyphosate), a salt, adduct or ester thereof, or a compound which is converted to glyphosate in plant tissues or which otherwise provides glyphosate ion. Glyphosate salts that can be used according to this invention include but are not restricted to alkali metal, for example sodium and potassium, salts; ammonium salt; alkylamine, for example dimethylamine and isopropylamine, salts; alkanolamine, for example ethanolamine, salts; alkylsulfonium, for example trimethylsulfonium, salts; sulfoxonium salts; and mixtures thereof. The herbicidal compositions sold by Monsanto Company as ROUNDUP® and ACCORD® contain the monoisopropylamine (IPA) salt of N-phosphonomethylglycine. The herbicidal compositions sold by Monsanto Company as ROUNDUP® Dry and RIVAL® contain the monoammonium salt of N-phosphonomethylglycine. The herbicidal composition sold by Monsanto Company as ROUNDUP® Geoforce contains the monosodium salt of N-phosphonomethylglycine. The herbicidal composition sold by Zeneca as TOUCHDOWN® contains the trimethylsulfonium salt of N-phosphonomethylglycine. The herbicidal properties of N-phosphonomethylglycine and its derivatives were first discovered by Franz, then disclosed and patented in U.S. Patent 3,799,758, issued March 26, 1974. A number of herbicidal salts of N-phosphonomethylglycine were patented by Franz in U.S. Patent 4,405,531, issued September



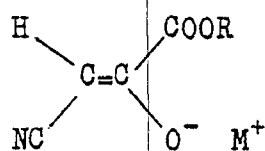
(XX)

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(XXI)

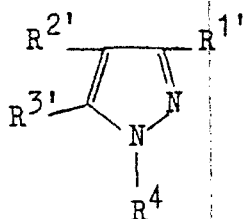
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(XXIV)

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(XXIV)

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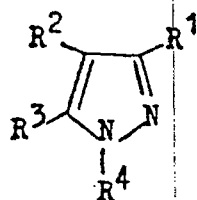
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Claims

1. An N-phenylpyrazole derivative of the general formula:

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(I)

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wherein R¹ represents a cyano or nitro group, a halogen atom, or an acetyl or formyl group;
 R² represents a group R⁵SO₂, R⁵SO, or R⁵S in which R⁵ represents a straight- or branched-chain alkyl,
 alkenyl or alkynyl group containing up to 4 carbon atoms which may be unsubstituted or substituted by
 one or more halogen atoms which may be the same or different;
 R³ represents a hydrogen atom or an amino group -NR⁶R⁷ wherein R⁶ and R⁷, which may be the same or

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bracken (*Pteridium aquilinum*)

blackberry (*Rubus* spp.)

gorse (*Ulex europaeus*)

5 Thus, the method of the present invention, as it pertains to glyphosate herbicide, can be useful on any of the above species.

Effectiveness in greenhouse tests, usually at exogenous chemical rates lower than those normally effective in the field, is a proven indicator of consistency of field performance at normal use rates.

However, even the most promising composition sometimes fails to exhibit enhanced performance in individual greenhouse tests. As illustrated in the Examples herein, a pattern of enhancement emerges
10 over a series of greenhouse tests; when such a pattern is identified this is strong evidence of biological enhancement that will be useful in the field.

The first excipient substance in compositions of the present invention is selected from the class of amphiphilic liposome-forming substances. These include various lipids of synthetic, animal, or plant
15 origin, including phospholipids, ceramides, sphingolipids, dialkyl surfactants, and polymeric surfactants. A variety of these materials are known to those skilled in the art, and are commercially available. Lecithins are particularly rich in phospholipids and can be derived from a number of plant and animal sources. Soybean lecithin is one particular example of a relatively inexpensive commercially available material that includes such substances.

20 Many other substances have been described which can be used to form liposomes; the present invention includes compositions comprising any such liposome-forming substances, so long as other requirements set out above are met, and use of such compositions for enhancing biological effectiveness of exogenous chemicals applied to foliage of plants. For example, US Patent No. 5,580,859, incorporated here by reference, discloses liposome-forming substances having a cationic group,
25 including N-(2,3-di-(9-(Z)-octadecenyl-oxy))-prop-1-yl-N,N,N-trimethylammonium chloride (DOTMA) and 1,2-bis(oleoyloxy)-3-(trimethylammonio)propane (DOTAP). Liposome-forming substances which are not themselves cationic, but do contain a cationic group as part of the hydrophilic moiety, include for example dioleoylphosphatidylcholine (DOPC) and dioleoylphosphatidylethanolamine (DOPE). Any of these liposome-forming substances can be used with or without the addition of cholesterol.

30 These substances contain portions that are hydrophilic and hydrophobic within the same molecule. They have the ability to self-assemble in aqueous solution or dispersion into structures that are more complex than simple micelles. The nature of the aggregate that will be formed can be related to the critical packing parameter P by the following equation:

$$P = V / lA$$

35 where V is the volume of the hydrophobic tail of the molecule, l is the effective length of the hydrophobic tail, and A is the area occupied by the hydrophilic headgroup in the surface of the aggregate.

different, each represent a hydrogen atom or a straight- or branched-chain alkyl, alkenylalkyl or alkynylalkyl group containing up to 5 carbon atoms, a formyl group, a straight- or branched-chain alkanoyl group (which contains from 2 to 5 carbon atoms and which may be optionally substituted by one or more halogen atoms) or R⁶ and R⁷ together with the nitrogen atom to which they are attached form a 5 or 6 membered cyclic imide, or represents a straight- or branched-chain alkoxy carbonyl group (which contains from 2 to 5 carbon atoms and is unsubstituted or substituted by one or more halogen atoms), or R³ represents a straight or branched-chain alkoxy methyleneamino group containing from 2 to 5 carbon atoms which may be unsubstituted or substituted on methylene by a straight or branched-chain alkyl group containing from 1 to 4 carbon atoms or represents a halogen atom; and R⁴ represents a phenyl group substituted in the 2-position by a fluorine, chlorine, bromine or iodine atom; in the 4- position by a straight- or branched-chain alkyl or alkoxy group containing from 1 to 4 carbon atoms, which may be unsubstituted or substituted by one or more halogen atoms which may be the same or different, or a chlorine or bromine atom; and optionally in the 6-position by a fluorine, chlorine, bromine or iodine atom, with the exclusion of the compound wherein R¹ represents cyano, R² represents methanesulphonyl, R³ represents amino and R⁴ represents 2,6-dichloro-4-trifluoromethylphenyl.

2. A compound according to claim 1 wherein R¹ is other than a formyl group and neither R⁶ nor R⁷ represents an alkenylalkyl or alkynylalkyl group.

3. A compound according to claim 1 wherein R² represents an alkylsulphonyl/sulphinyl/thio group which is optionally halogen substituted and contains from 1 to 4 carbon atoms, or an alkenyl- or alkynyl-sulphonyl/sulphinyl/thio group which is optionally halogen substituted and contains up to 4 carbon atoms, R³ represents the hydrogen atom, an amino or methylamino group and R¹ represents a halogen atom or a cyano or nitro group.

4. A compound according to claim 3 wherein R¹ represents a cyano or nitro group.

5. A compound according to any one of the preceding claims wherein R⁴ contains a trifluoromethyl or trifluoromethoxy group and R² represents an optionally halogenated alkylsulphonyl/sulphinyl/thio group containing from 1 to 4 carbon atoms.

6. A compound according to claim 5 wherein R² represents a trifluoromethylthio, trifluoromethylsulphinyl or trifluoromethylsulphonyl group.

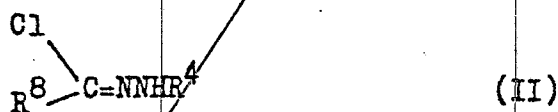
7. A compound according to any one of the preceding claims wherein R⁴ represents a 2,4,6-trichloro-, 2,6-dichloro-4-difluoromethoxy-, 2-chloro-4-trifluoromethyl-, 2-bromo-6-chloro-4-trifluoromethyl-, 2,6-dibromo-4-trifluoromethyl- or 2-bromo-4-trifluoromethyl-phenyl group.

8. A compound according to any one of claims 1 to 6 wherein R⁴ represents a 2,6-dichloro-4-trifluoromethyl- or 2,6-dichloro-4-trifluoromethoxy-phenyl group.

9. A compound according to claim 1 hereinbefore identified as any one of compounds 1 to 101.

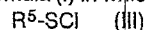
10. A process for the preparation of a compound according to claim 1 which comprises:

(a) when R² represents an R⁵SO₂, R⁵SO or R⁵S group, R³ represents the unsubstituted amino group and R¹ represents a cyano or acetyl group, the reaction of a compound of general formula:



wherein R⁸ represents a cyano or acetyl group and R⁴ is as defined in claim 1, with a compound of the general formula R²CH₂CN, wherein R² is as defined in claim 1;

(b) when R² represents an R⁵S group and R³ represents an amino group -NR⁶R⁷ wherein R⁶ and R⁷ each represents a hydrogen atom or a straight- or branched-chain alkyl, alkenylalkyl or alkynylalkyl group as defined in claim 1, the reaction of a compound corresponding to general formula (I) in which R² is replaced by the hydrogen atom with a compound of the general formula:-



wherein R⁵ is as defined in claim 1

(c) when R¹ represents a chlorine or fluorine atom, R² represents an R⁵SO₂, R⁵SO or R⁵S group, and R³ represents an amino group, by the reaction of a compound of the general formula:



wherein X and Y both represent chlorine atoms or both represent fluorine atoms, with a

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The most probable self-assembled structures are spherical micelles when P is less than $1/3$, rodlike micelles when P is between $1/3$ and $1/2$, lamellar when P is between 1 and $1/2$, and inverse structures when P is greater than 1 . The preferred materials in the present invention have P greater than $1/3$.

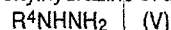
Cationic liposome-forming substances having a hydrophobic moiety comprising two hydrocarbyl chains are accompanied by a counterion (anion), identified as Z in formulas I, II and III above. Any suitable anion can be used, including agriculturally acceptable anions such as hydroxide, chloride, bromide, iodide, sulfate, phosphate and acetate. In a specific embodiment where the exogenous chemical has a biologically active anion, that anion can serve as the counterion for the liposome-forming substance. For example, glyphosate can be used in its acid form together with the hydroxide of a cationic liposome-forming substance such as a compound of formula I.

Compounds of formula I known in the art to be liposome-forming include distearyldimethylammonium chloride and bromide (also known in the art as DODAC and DODAB respectively). Compounds of formula II known in the art to be liposome-forming include DOTMA referenced above and dimyristoxypropyldimethylhydroxyethylammonium bromide (DMRIE). Compounds of formula III known in the art to be liposome-forming include dioleoyloxy-3-(dimethylammonio)propane (DODAP) and DOTAP referenced above. Compounds of formula IV known in the art to be liposome-forming include DOPC and DOPE, both referenced above.

In many liposome-forming substances known in the art, the hydrophobic hydrocarbyl chains are unsaturated, having one or more double bonds. Particularly commonly used in the pharmaceutical art are dioleyl or dioleoyl compounds. A potential problem with these is that in an oxidizing environment they become oxidized at the site of the double bond. This can be inhibited by including in the formulation an antioxidant such as ascorbic acid. Alternatively the problem can be avoided by use of liposome-forming substances wherein a high proportion of the hydrophobic hydrocarbyl chains are fully saturated. Thus in a composition of the present invention, from about 40 to 100 percent of the hydrocarbyl chains (R^1 and R^2 in formulas I-IV) in the composition are saturated straight-chain alkyl groups. Particularly preferred compositions use liposome-forming substances in which R^1 and R^2 , together with the adjacent CH_2 or CO groups shown in formulas I-IV, both form palmityl (cetyl) or palmitoyl or, alternatively, both form stearyl or stearoyl groups.

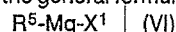
Phospholipids, because of their low cost and favorable environmental properties, are particularly favored among liposome-forming substances in the method and compositions of the invention. Vegetable lecithins, such as soybean lecithin, are a rich source of phospholipids; however in vegetable lecithins a high proportion of the hydrophobic hydrocarbyl chains of the phospholipid compounds are typically unsaturated. One embodiment of compositions in accordance with the present invention comprises both saturated phospholipid and unsaturated phospholipid, with the weight ratio of saturated phospholipid to unsaturated phospholipid being greater than about 1:2. In various particularly preferred embodiments, (1) at least 50% by weight of the phospholipids are di- C_{12-22} -saturated alkanoyl

phenylhydrazine of the general formula:

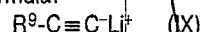


wherein R^4 is as defined in claim 1, or an acid addition salt thereof;

(d)(1) when R^2 represents an R^5S group, R^1 represents a chlorine, bromine, iodine or fluorine atom or a cyano or nitro group and R^3 represents an amino group, the reaction of a compound corresponding to general formula (I) in which R^2 is replaced by a thiocyanato group with a compound of the general formula:

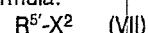


(wherein R^5 is as defined in claim 1 and X^1 represents a halogen atom) or a compound of the general formula:

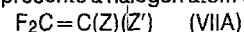


wherein $R^9-C \equiv C-$ corresponds to R^5 in formula (I);

(d)(2) when R^2 represents an R^5S group wherein R^5S is other than a 1-alkenylthio or 1-alkynylthio group, the reaction of a compound corresponding to general formula (I) in which R^2 is replaced by a thiocyanato group with a base or a reducing agent in the presence of a reagent of the general formula:

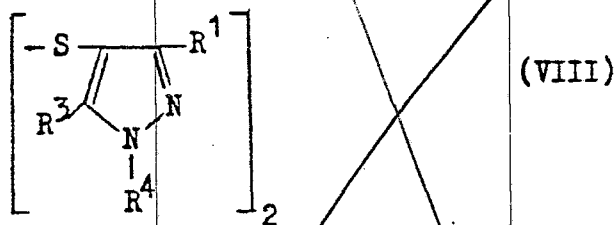


wherein R^5 is as defined in claim 1 for R^5 with the exclusion of 1-alkenyl and 1-alkynyl and X^2 represents a halogen atom or with a base in the presence of a compound of the general formula:



wherein Z represents a fluorine, chlorine or bromine atom and Z' is as defined for Z or represents the trifluoromethyl group;

(d)(3) when R^5S is other than a 1-alkenylthio or 1-alkynylthio group, by the reductive alkylation of a disulphide of the general formula:



wherein R^1 , R^3 and R^4 are as defined in claim 1 employing a reducing agent in the presence of a base and of a halide of general formula (VII) wherein R^5 is as hereinbefore defined;

(e) when R^2 represents an R^5SO or R^5SO_2 group, by the oxidation of the sulphur atom in a compound of general formula I wherein R^2 represents a group R^5S ;

(f) when R^1 represents a fluorine, chlorine, bromine or iodine atom or a cyano or nitro group, by the diazotisation of a compound corresponding to general formula (I) in which R^1 is replaced by an amino group and R^3 represents a hydrogen atom or an amino group, and conversion of the diazotised amino group R^1 by known methods into a fluorine, chlorine, bromine or iodine atom or a cyano or nitro group or when R^3 represents a halogen atom by the diazotisation of a compound of general formula (I) wherein R^3 represents an amino group and conversion of the diazotised amino group R^3 by known methods into a halogen atom;

(g) when R^1 represents a fluorine atom or a cyano group and R^3 represents a hydrogen atom or the amino group, the reaction of a halide of general formula (I) wherein R^1 represents a chlorine or bromine atom with an alkali metal fluoride or with a metal cyanide to convert the chlorine or bromine atom to a fluorine atom or a cyano group;

(h) when R^1 represents a nitro group and R^2 represents a group R^5SO_2 or R^5SO , by the reaction of a compound corresponding to general formula (I) in which R^1 is replaced by an unsubstituted amino group and R^2 is a group R^5SO_2 , R^5SO or R^5S , and R^3 represents a hydrogen atom or the amino group, with an oxidant to convert the unsubstituted amino group into a nitro group R^1 ;

(i) when R^1 represents the cyano group and R^3 represents a hydrogen atom or the amino group, by the dehydration of a compound corresponding to general formula (I) in which R^1 is replaced by the carbamoyl group;

(j) when R^1 is the acetyl group and R^3 represents a hydrogen atom or the amino group, by the reaction of a corresponding nitrile of formula (I) wherein R^1 is the cyano group, or of a corresponding ester wherein R^1 is replaced by an alkoxycarbonyl group CO_2R wherein R represents a straight- or branched-chain alkyl group containing from 1 to 6 carbon atoms, or of a carboxylic acid wherein R^1 is replaced by a carboxy group, with methyl lithium, or the reaction of a nitrile of formula (I) wherein R^1 is the cyano group or the ester wherein R^1 is replaced by an alkoxycarbonyl group CO_2R with a Grignard reagent CH_3MgX^3 wherein X^3 represents a halogen atom;

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phospholipid, (2) at least 50% by weight of the phospholipids are di-C₁₆₋₁₈-saturated alkanoyl phospholipid, (3) at least 50% by weight of the phospholipids are distearoyl phospholipid, (4) at least 50% by weight of the phospholipids are dipalmitoyl phospholipid, or (5) at least 50% by weight of the phospholipids are distearoyl phosphatidylcholine, dipalmitoyl phosphatidylcholine, or a mixture thereof.

5 Higher proportions of saturated alkanoyl phospholipids are generally found in lecithins of animal origin, such as for example egg yolk lecithin, than in vegetable lecithins. Illustratively, analysis of samples of egg yolk lecithin and soybean lecithin has shown 45% of acyl chains in egg yolk lecithin, and only 22% of acyl chains in soybean lecithin to be saturated alkanoyl chains.

Phospholipids are known to be chemically unstable, at least in acid media, where they tend to

10 degrade to their lyso-counterparts. Thus where phospholipids rather than more stable liposome-forming substances are used, it is usually preferable to adjust the pH of the composition upward. In the case of glyphosate compositions, the pH of a composition based on a mono-salt such as the monoisopropylammonium (IPA) salt is typically around 5 or lower. When phospholipids are used as the first excipient substance in a glyphosate composition of the invention, it will therefore be preferable to

15 raise the pH of the composition, for example to around 7. Any convenient base can be used for this purpose; it will often be most convenient to use the same base as used in the glyphosate salt, for example isopropylamine in the case of glyphosate IPA salt.

Compounds useful as the second excipient substance herein include quaternary ammonium compounds having formula V above. In compounds of formula V, R⁸ unless perfluorinated preferably

20 has from about 12 to about 18 carbon atoms. R⁸ is preferably perfluorinated, in which case it preferably has from about 6 to about 12 carbon atoms. Preferably n is 3. R⁹ groups are preferably methyl.

Sulfonylamino compounds of formula V are especially preferred. Suitable examples include 3-(((heptadecafluorooctyl)sulfonyl)amino)-N,N,N-trimethyl-1-propaminium iodide, available for

example as Fluorad FC-135 from 3M Company, and the corresponding chloride. It is believed that

25 Fluorad FC-754 of 3M Company is the corresponding chloride.

Derivatives of Fluorad FC-754, herein described as "FC-acetate" and "FC-salicylate," have been prepared by the following procedure. (1) The solvent in a sample of Fluorad FC-754 is gently evaporated off by heating in a glass beaker at 70-80°C, to leave a solid residue. (2) The solid residue is allowed to cool to room temperature. (3) A 1 g aliquot of the residue is placed in a centrifuge tube and

30 dissolved in 5 ml isopropanol. (4) A saturated solution of potassium hydroxide (KOH) is prepared in isopropanol. (5) This solution is added drop by drop to the solution of FC-754 residue; this results in formation of a precipitate and addition of KOH solution continues until no further precipitate forms. (6) The tube is centrifuged at 4000 rpm for 5 minutes. (7) More KOH solution is added to check if precipitation is complete; if not, the tube is centrifuged again. (8) The supernatant is decanted into

35 another glass tube. (9) A saturated solution of acetic acid (or salicylic acid) is prepared in isopropanol. (10) This solution is added to the supernatant in an amount sufficient to lower pH to 7. (11) Isopropanol

(k) when R^1 represents the acetyl group and R^3 is as defined above, by the oxidation of an alcohol corresponding to general formula (I) wherein R^1 is replaced by a hydroxyethyl group, with an oxidant;

(l) when R^1 represents a formyl group and R^3 is as defined above by the reaction of a corresponding nitrile of general formula (I) wherein R^1 represents a cyano group with a reducing agent followed by acid hydrolysis or with Raney nickel in formic acid to convert the cyano group to a formyl group;

(m) the conversion by known methods of a compound of general formula (I) wherein R^3 represents an amino group NR^6R^7 into a compound of general formula (I) wherein R^3 represents a different amino group NR^6R^7 ;

(n) when R^3 represents a straight- or branched-chain alkoxyethyleneamino group containing from 2 to 5 carbon atoms which may be unsubstituted or substituted on methylene by a straight- or branched-chain alkyl group containing from 1 to 4 carbon atoms, by the reaction of a compound of general formula (I) wherein R^3 represents the unsubstituted amino group with a trisalkoxyalkane;

(o) when R^3 represents a group $-NHCH_2R^{16}$ wherein R^{16} represents the hydrogen atom or a straight- or branched-chain alkyl group containing from 1 to 4 carbon atoms, by the reaction of a compound of general formula (I) wherein R^3 represents a group $-N=C(OR^{17})R^{16}$ wherein R^{17} represents a straight- or branched-chain alkyl group containing from 1 to 4 carbon atoms with a reducing agent;

(p) when R^1 represents a formyl, acetyl, cyano or nitro group, and R^3 represents a fluorine atom, by a halogen exchange reaction with a compound of general formula (I) wherein R^3 represents a chlorine or bromine atom;

(q) when R^3 represents a hydrogen atom by the reaction of a compound of general formula (I) wherein R^3 represents an amino group with a diazotising agent in a solvent at ambient to reflux temperature to convert the amino group R^3 to a hydrogen atom;

(r) when R^1 represents a cyano or nitro group, R^2 is a group R^5SO_2 , R^6 and R^7 each represents a straight- or branched-chain alkyl, alkenylalkyl or alkynylalkyl group containing up to 5 carbon atoms and R^7 may also represent a hydrogen atom, by the reaction of a compound of general formula (I) wherein R^3 represents a halogen atom with the corresponding amine within general formula R^6R^7NH , or with dimethylhydrazine when R^6 and R^7 are both methyl;

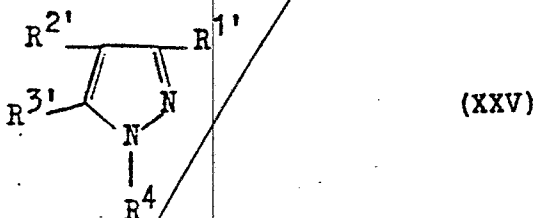
optionally followed by the conversion of a compound of general formula (I) thus obtained into another compound of general formula (I).

11. An arthropodocidal, plant nematocidal, anthelmintic or anti-protozoal composition which comprises a compound of general formula (I) in association with one or more compatible diluents or carriers.

12. A method for the control of arthropod, plant nematode, helminth or protozoal pests at a locus which comprises treatment of the locus with an effective amount of the compound according to claim 1.

13. A compound of general formula (I) as defined in claim 1 for use in the manufacture of a medicament for the treatment of an arthropod, helminth or protozoal infection.

14. A compound of the general formula:



wherein $R^{2'}$ is as defined in claim 1 for R^2 or represents the hydrogen atom, a thiocyanato, formyl, cyano or carboxy group, a straight- or branched-chain alkoxy carbonyl group containing from 2 to 7 carbon atoms or the dithio group (which joins two pyrazole rings), $R^{3'}$ is as defined in claim 1 for R^3 or represents the diphenoxycarbonylamino group, and $R^{1'}$ is as defined in claim 1 for R^1 or represents the amino, 1-hydroxyethyl, carboxy or carbamoyl group or a straight- or branched-chain alkoxy carbonyl or alkoxy carbonylamino group containing from 2 to 7 carbon atoms,

with the exclusion of compounds of general formula (I) as defined in claim 1 and of those compounds of general formula (XXV) wherein R^4 represents 2,6-dichloro-4-trifluoromethylphenyl, $R^{2'}$ represents the cyano group, $R^{1'}$ represents the cyano group and $R^{3'}$ represents the amino, acetamido, dichloroacetamido, t-butylcarbonylamino, propionamido, pentanamido, bis(ethoxycarbonyl)amino, ethoxycarbonylamino, methylamino or ethylamino group,

or $R^{1'}$ represents the chlorine atom and $R^{3'}$ represents the amino, t-butylcarbonylamino, bis(ethoxycarbonyl)amino or ethoxycarbonylamino group,

or $R^{1'}$ represents a bromine or iodine atom or an amino or ethoxycarbonyl group and $R^{3'}$ represents the amino group,

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phospholipid, (2) at least 50% by weight of the phospholipids are di-C₁₆₋₁₈-saturated alkanoyl phospholipid, (3) at least 50% by weight of the phospholipids are distearoyl phospholipid, (4) at least 50% by weight of the phospholipids are dipalmitoyl phospholipid, or (5) at least 50% by weight of the phospholipids are distearoyl phosphatidylcholine, dipalmitoyl phosphatidylcholine, or a mixture thereof.

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Phospholipids are known to be chemically unstable, at least in acid media, where they tend to

10 degrade to their lyso-counterparts. Thus where phospholipids rather than more stable liposome-forming substances are used, it is usually preferable to adjust the pH of the composition upward. In the case of glyphosate compositions, the pH of a composition based on a mono-salt such as the monoisopropylammonium (IPA) salt is typically around 5 or lower. When phospholipids are used as the first excipient substance in a glyphosate composition of the invention, it will therefore be preferable to

15 raise the pH of the composition, for example to around 7. Any convenient base can be used for this purpose; it will often be most convenient to use the same base as used in the glyphosate salt, for example isopropylamine in the case of glyphosate IPA salt.

Compounds useful as the second excipient substance herein include quaternary ammonium compounds having formula V above. In compounds of formula V, R⁸ unless perfluorinated preferably

20 has from about 12 to about 18 carbon atoms. R⁸ is preferably perfluorinated, in which case it preferably has from about 6 to about 12 carbon atoms. Preferably n is 3. R⁹ groups are preferably methyl.

Sulfonylamino compounds of formula V are especially preferred. Suitable examples include 3-(((heptadecafluorooctyl)sulfonyl)amino)-N,N,N-trimethyl-1-propaminium iodide, available for

25 example as Fluorad FC-135 from 3M Company, and the corresponding chloride. It is believed that Fluorad FC-754 of 3M Company is the corresponding chloride.

Derivatives of Fluorad FC-754, herein described as "FC-acetate" and "FC-salicylate," have been prepared by the following procedure. (1) The solvent in a sample of Fluorad FC-754 is gently evaporated off by heating in a glass beaker at 70-80°C, to leave a solid residue. (2) The solid residue is allowed to cool to room temperature. (3) A 1 g aliquot of the residue is placed in a centrifuge tube and

30 dissolved in 5 ml isopropanol. (4) A saturated solution of potassium hydroxide (KOH) is prepared in isopropanol. (5) This solution is added drop by drop to the solution of FC-754 residue; this results in formation of a precipitate and addition of KOH solution continues until no further precipitate forms. (6) The tube is centrifuged at 4000 rpm for 5 minutes. (7) More KOH solution is added to check if precipitation is complete; if not, the tube is centrifuged again. (8) The supernatant is decanted into

35 another glass tube. (9) A saturated solution of acetic acid (or salicylic acid) is prepared in isopropanol. (10) This solution is added to the supernatant in an amount sufficient to lower pH to 7. (11) Isopropanol

or R^1 represents the fluorine atom and R^3 represents the hydrogen atom or the amino group, or R^1 represents a nitro, amino, t-butoxycarbonylamino or ethoxycarbonyl group and R^3 represents the hydrogen atom;

R^4 represents a 2,4,6-trichlorophenyl, 2-chloro-4-trifluoromethylphenyl or 2,6-dichloro-4-trifluoromethoxyphenyl group, R^2 represents the cyano group, R^1 represents the cyano group and R^3 represents the amino group;

R^4 represents a 2,6-dichloro-4-trifluoromethoxyphenyl group, R^2 represents the cyano group, R^1 represents the chlorine atom and R^3 represents the amino group; and R^4 represents the 2,6-dichloro-4-trifluoromethylphenyl group, R^2 represents the methanesulphonyl group, R^1 represents a carboxy, carbamoyl or ethoxycarbonyl group and R^3 represents the amino group.

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is evaporated from this neutralized solution by heating at 60°C until completely dry. (12) The residue (either the acetate or salicylate salt) is dissolved in a suitable amount of water and is then ready for use.

Another class of quaternary ammonium compounds useful as the second excipient substance in the present invention has the formula



where R^{16} , R^{17} , R^{18} and R^{19} are independently C_{3-6} alkyl groups and Q is a suitable anion, such as for example hydroxide, chloride, bromide, iodide, sulfate, phosphate or acetate. In preferred compounds of formula VIII all R groups are the same. Particularly preferred compounds of formula VIII are tetrabutylammonium salts. Where the exogenous chemical comprises a biologically active anion, a salt of formula VIII where Q is that anion is an option providing both the exogenous chemical and second excipient substance. An example is the tetrabutylammonium salt of glyphosate.

Other quaternary ammonium compounds that may be useful include compounds having a single C_{12-22} hydrocarbyl group and three groups selected from benzyl or C_{1-4} alkyl groups attached to the quaternary nitrogen atom. Specific examples include cetyltrimethylammonium bromide and benzalkonium chloride.

Another class of compound useful as the second excipient substance is an amide or ester of formula VII above.

R^{14} in formula VII is preferably aliphatic and has about 7 to about 21 carbon atoms, more preferably about 13 to about 21 carbon atoms. It is especially preferred that R^{14} be a saturated straight-chain alkyl group. R^{15} is preferably an aliphatic group having 1-6 carbon atoms, more preferably alkyl or alkenyl having 2-4 carbon atoms. An especially preferred compound of formula VII for use as the second excipient substance is butyl stearate.

As compounds of formula VII, including butyl stearate, are generally oily liquids, aqueous compositions containing them are typically emulsions having at least one aqueous phase and at least one oil phase, with the compound of formula VII being present predominantly in the oil phase. Such emulsions may be water-in-oil, oil-in-water or water-in-oil-in-water (W/O/W) multiple emulsions.

Compositions in accordance with the present invention are typically prepared by combining water, the exogenous chemical and the first excipient substance. Where the first excipient substance is one that disperses readily in water, simple mixing with mild agitation may be sufficient. However, most liposome-forming substances including most forms of lecithin require high shear to disperse in water, and in such cases it is presently preferred to sonicate or microfluidize the liposome-forming first excipient substance in water. This can be done before or after a second excipient substance and/or the exogenous chemical is added. The sonication or microfluidization will generally produce liposomes or other aggregate structures other than simple micelles. The precise nature, including average size, of liposomes or other aggregates depends among other things on the energy input during sonication or microfluidization. Higher energy input generally results in smaller liposomes. Although it is possible to

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(54) Title: NEW PROCESSES FOR PREPARING PESTICIDAL INTERMEDIATES			
(57) Abstract The invention relates to a process for preparing a compound of general formula (I) which is useful as an intermediate in the synthesis of pesticidally active compounds.			
		(I)	

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entrap or otherwise bind loosely or tightly the exogenous chemical in or on liposomes or with other supramolecular aggregates, the exogenous chemical does not need to be so entrapped or bound, and in fact the present invention is effective when the exogenous chemical is not entrapped or bound in the aggregates at all.

5 In a particular embodiment of the invention, the liposomes or other aggregates have an average diameter of at least 20 nm, more preferably at least 30 nm. Average liposome diameters can be determined by light scattering techniques.

The concentrations of the various components will vary, in part depending on whether a concentrate is being prepared that will be further diluted before spraying onto a plant, or whether a
10 solution or dispersion is being prepared that can be sprayed without further dilution.

In an aqueous glyphosate formulation that includes a dialkyl surfactant, for example a cationic dialkyl surfactant of formula I, suitable concentration ranges are: glyphosate 0.1 - 400 grams acid equivalent (a.e.)/liter, and dialkyl surfactant 0.001 - 10% by weight. In an aqueous glyphosate formulation using a cationic fluoro-organic surfactant and lecithin, suitable concentrations can be:
15 glyphosate 0.1 - 400 g a.e./l, fluoro-organic surfactant 0.001 - 10% by weight, and egg yolk lecithin 0.001 - 10% by weight.

In solid glyphosate formulations, higher concentrations of ingredients are possible because of the elimination of most of the water.

Weight/weight ratios of ingredients may be more important than absolute concentrations. For
20 example, in a glyphosate formulation containing egg yolk lecithin and a cationic fluoro-organic surfactant, the ratio of lecithin to glyphosate a.e. is preferably in the range from about 1:3 to about 1:100. It is generally preferred to use a ratio of lecithin to glyphosate a.e. close to as high as can be incorporated in the formulation while maintaining stability, in the presence of an amount of the fluoro-organic surfactant sufficient to give the desired enhancement of herbicidal effectiveness. For example, a
25 lecithin/glyphosate a.e. ratio in the range from about 1:3 to about 1:10 will generally be found useful, although lower ratios, from about 1:10 to about 1:100 can have benefits on particular weed species in particular situations. The ratio of fluoro-organic surfactant, when present, to glyphosate a.e. is likewise preferably in the range from about 1:3 to about 1:100. Because fluoro-organic surfactants tend to have relatively high cost, it will generally be desirable to keep this ratio as low as possible consistent with
30 achieving the desired herbicidal effectiveness..

The ratio of fluoro-organic surfactant, where present, to lecithin is preferably in the range from about 1:10 to about 10:1, more preferably in the range from about 1:3 to about 3:1 and most preferably around 1:1. The ranges disclosed herein can be used by one of skill in the art to prepare compositions of the invention having suitable concentrations and ratios of ingredients. Preferred or optimum
35 concentrations and ratios of ingredients for any particular use or situation can be determined by routine experimentation.

New Processes For Preparing
Pesticidal Intermediates

5 This invention relates to a process for preparing certain cyanomethylpropane derivatives and the use of these compounds in the synthesis of pesticides and pesticide intermediates.

10 Ethyl 2,3-dicyanopropionate was first prepared and characterised by Higson and Thorpe (J.Chem.Soc. 89, 1460 (1906)) who obtained the material in good yield (70-81%) by reaction of formaldehyde cyanohydrin with the sodium salt of ethyl cyanoacetate. Dickinson {J. Am. Chem. Soc. 82, 6132 (1960)} repeated this work. This method of preparing the dicyanopropionate suffers from a significant drawback in that it is first necessary to isolate the intermediate formaldehyde cyanohydrin. This highly water soluble
15 cyanohydrin is obtained by lengthy continuous extraction and has a limited stability, often decomposing violently upon attempted distillation. Furthermore, this reaction requires care given the risk of formation of dimeric side-products. The preparation of dicyanopropionates has also been described by Whiteley and
20 Marianelli (Synthesis (1978), 392) with the process leading to 2,3-disubstituted succinodinitriles from the cyanoacetate, an aldehyde (a 1 to 3 carbon alkylaldehyde or benzaldehyde) and potassium cyanide via 3-substituted-2,3- dicyanopropionates (which were not isolated). However, the yield decreases dramatically from isobutyraldehyde to
25 acetaldehyde. In the same manner Smith and Horwitz (J. Am. Chem. Soc. 1949, 71, 3418) described the same reaction with a ketone with a yield of 70%. This prior art therefore teaches that yields improve with increasing size of group adjacent to the carbonyl group.

30 In one aspect the present invention seeks to provide a process for preparing cyanomethyl propane derivatives satisfying one or more of the following criteria:

- avoiding the use of formaldehyde cyanohydrin;
- avoiding the dimerisation side reaction;

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Although the combination of the components might be done in a tank mix, it is preferred in the present invention that the combination be made further in advance of the application to the plant, in order to simplify the tasks required of the person who applies the material to plants. We have found, however, that in some cases the biological effectiveness of a liposome-containing composition prepared from scratch as a dilute spray composition is superior to that of a composition having the same ingredients at the same concentrations but diluted from a previously prepared concentrate formulation.

Although various compositions of the present invention are described herein as comprising certain listed materials, in some preferred embodiments of the invention the compositions consist essentially of the indicated materials.

Optionally, other agriculturally acceptable materials can be included in the compositions. For example, more than one exogenous chemical can be included. Also, various agriculturally acceptable adjuvants can be included, whether or not their purpose is to directly contribute to the effect of the exogenous chemical on a plant. For example, when the exogenous chemical is a herbicide, liquid nitrogen fertilizer or ammonium sulfate might be included in the composition. As another example, stabilizers can be added to the composition. In some instances it might be desirable to include microencapsulated acid in the composition, to lower the pH of a spray solution on contact with a leaf. One or more surfactants can also be included. Surfactants mentioned here by trade name, and other surfactants that can be useful in the method of the invention, are indexed in standard reference works such as McCutcheon's Emulsifiers and Detergents, 1997 edition, Handbook of Industrial Surfactants, 2nd Edition, 1997, published by Gower, and International Cosmetic Ingredient Dictionary, 6th Edition, 1995.

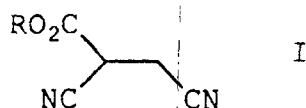
The compositions of the present invention can be applied to plants by spraying, using any conventional means for spraying liquids, such as spray nozzles, atomizers, or the like. Compositions of the present invention can be used in precision farming techniques, in which apparatus is employed to vary the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

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

Many exogenous chemicals (including glyphosate herbicide) must be taken up by living tissues of the plant and translocated within the plant in order to produce the desired biological (e.g., herbicidal)

obtaining the required product directly in high yield and with high purity.

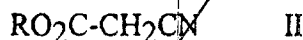
Therefore the present invention provides a process for preparing a compound of formula (I):



wherein

R represents straight- or branched- chain alkyl having up to 18 carbon atoms; or a salt thereof;

which comprises the reaction of a cyanoacetate of formula (II):-



wherein R is as defined above, with a cyanide salt and formaldehyde or a source thereof.

Preferably R represents straight- or branched-chain alkyl having from 1 to 6 carbon atoms and most preferably R represents ethyl.

Suitable salts of cyanide include metal salts and organic salts (e.g. tetra-alkylammonium cyanides such as tetrabutylammonium cyanide). Preferably the cyanoacetate of formula (II) reacts with an alkali or alkaline earth metal cyanide salt, with alkali metal cyanide salts being especially suitable for use in the present invention, particularly potassium cyanide or sodium cyanide. The product may conveniently be isolated as the alkaline earth metal or alkali metal salt. Alternatively, the reaction mixture is acidified, for example with a mineral acid such as sulphuric acid or hydrochloric acid, to give the compound of formula (I). Where a compound of formula (I) above is desired (rather than a salt thereof) high yields are generally obtained when the reaction mixture is acidified without the addition of water.

Whilst formaldehyde itself can be used in the reaction it is more convenient to use the polymerised form known as paraformaldehyde $[(\text{HCOH})_n]$, available for example from Aldrich Chemical Company.

The reaction is generally performed using about 1 molar equivalent of a compound of formula (II); about 0.95 to 1.0 molar

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effect. Thus, it is important that a herbicidal composition not be applied in such a manner as to excessively injure and interrupt the normal functioning of the local tissue of the plant so quickly that translocation is reduced. However, some limited degree of local injury can be insignificant, or even beneficial, in its impact on the biological effectiveness of certain exogenous chemicals.

EXAMPLES

In the following Examples illustrative of the invention, greenhouse tests were conducted to evaluate relative herbicidal effectiveness of glyphosate compositions. Compositions included for comparative purposes included the following:

Formulation B: which consists of 41% by weight of glyphosate IPA salt in aqueous solution.

This formulation is sold in the USA by Monsanto Company under the ACCORD® trademark.

Formulation C: which consists of 41% by weight of glyphosate IPA salt in aqueous solution with a coformulant (15% by weight) of a surfactant (MON 0818 of Monsanto Company) based on polyoxyethylene (15) tallowamine. This formulation is sold in Canada by Monsanto Company under the ROUNDUP® trademark.

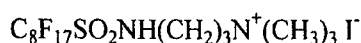
Formulation J: which consists of 41% by weight of glyphosate IPA salt in aqueous solution, together with surfactant. This formulation is sold in the USA by Monsanto Company under the ROUNDUP® ULTRA trademark.

Formulations B, C and J contain 356 grams of glyphosate acid equivalent per liter (g a.e./l).

Various proprietary excipients were used in compositions of the Examples. They may be identified as follows:

Trade name	Manufacturer	Chemical description
Fluorad FC-135	3M	fluorinated alkyl quaternary ammonium iodide
MON 0818	Monsanto	tallowamine 15EO-based surfactant

Fluorad FC-135, though defined only generically as above in 3M product literature and in standard directories, has been specifically identified as



in a paper by J. Linert & J. N. Chasman of 3M, titled "The effects of fluorochemical surfactants on recoatability" in the December 20, 1993 issue of American Paint & Coatings Journal, and reprinted as a trade brochure by 3M.

Where a proprietary excipient is a surfactant supplied as a solution in water or other solvent, the amount to be used was calculated on a true surfactant basis, not an "as is" basis. For example, Fluorad FC-135 is supplied as 50% true surfactant, together with 33% isopropanol and 17% water; thus to provide a composition containing 0.1% w/w Fluorad FC-135 as reported herein, 0.2 g of the product as supplied was included in 100 g of the composition. The amount of lecithin, however, is always reported herein on an "as is" basis, regardless of the content of phospholipid in the lecithin sample used.

equivalents of cyanide salt; and about 1 molar equivalent of formaldehyde compound (based on the formaldehyde content).

The reaction may be carried out in the presence of a solvent. Preferably, the reaction is performed in a solvent medium which is usually an alcoholic medium or dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), dioxan, tetrahydrofuran (THF) or dimethoxyethane. Especially preferred solvents are C₁-C₆ alcohols such as methanol or, most preferably, anhydrous ethanol. Although the temperature of the reaction is not critical the reaction will normally be performed from about 0 to about 120°C or at the reflux temperature of the solvent. Generally best results are obtained by introducing the formaldehyde source after the other reactants have been combined.

The reaction generally takes place under substantially anhydrous conditions (it being understood that the reaction proceeds with the formation of one equivalent of water), as in the event of prolonged exposure to aqueous conditions, there is a risk that the ester group of the compound of formula (I) will undergo hydrolysis (due to the basic conditions arising during the reaction) to the corresponding acid of formula (I) (in which R is replaced by hydrogen) and subsequently undergo decarboxylation to give 1,2-dicyanoethane.

The compound of formula (I) is useful in the preparation of pesticidally active compounds, for example as described in European Patent Publication Nos. 0295117 and 0234119, and WO93/06089.

In particular, the process of the invention may form part of an *in situ* preparation of another pesticidal intermediate and in a further aspect the invention provides a process for the preparation of a compound of formula (III):

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Spray compositions of the Examples contained an exogenous chemical, such as glyphosate IPA salt, in addition to the excipient ingredients listed. The amount of exogenous chemical was selected to provide the desired rate in grams per hectare (g/ha) when applied in a spray volume of 93 l/ha. Several exogenous chemical rates were applied for each composition. Thus, except where otherwise indicated, when spray compositions were tested, the concentration of exogenous chemical varied in direct proportion to exogenous chemical rate, but the concentration of excipient ingredients was held constant across different exogenous chemical rates.

Concentrate compositions were tested by dilution, dissolution or dispersion in water to form spray compositions. In these spray compositions prepared from concentrates, the concentration of excipient ingredients varied with that of exogenous chemical.

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

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

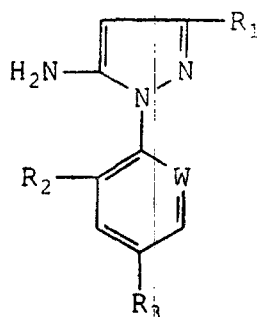
The plants were maintained for the duration of the test in the greenhouse where they received a minimum of 14 hours of light per day. If natural light was insufficient to achieve the daily requirement, artificial light with an intensity of approximately 475 microeinsteins was used to make up the difference. Exposure temperatures were not precisely controlled but averaged about 27°C during the day and about 18°C during the night. Plants were sub-irrigated throughout the test to ensure adequate soil moisture levels.

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

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

Treatments were made using dilute aqueous compositions. These could be prepared as spray compositions directly from their ingredients, or by dilution with water of preformulated concentrate compositions.

For evaluation of herbicidal effectiveness, all plants in the test were examined by a single practiced technician, who recorded percent inhibition, a visual measurement of the effectiveness of each treatment by comparison with untreated plants. Inhibition of 0% indicates no effect, and inhibition of 100% indicates that all of the plants are completely dead. Inhibition of 85% or more is in most cases

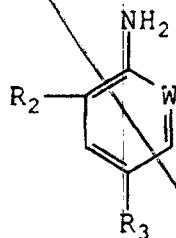


(III)

wherein R₁ is cyano; W is nitrogen or -CR₄; R₂ and R₄ independently represent halogen; and R₃ represents halogen, haloalkyl (preferably trifluoromethyl), haloalkoxy (preferably trifluoromethoxy) or -SF₅; which process comprises:

(a) reacting a cyanoacetate of formula (II) as defined above, with a cyanide salt and formaldehyde or a source thereof, to give a compound of formula (I) as defined above; and

(b) reacting the compound of formula (I) thus obtained with the diazonium salt of a compound of formula (IV):



(IV)

wherein W, R₂ and R₃ are as defined above, to give a compound of formula (V):

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considered acceptable for normal herbicidal use; however in greenhouse tests such as those of the Examples it is normal to apply compositions at rates which give less than 85% inhibition, as this makes it easier to discriminate among compositions having different levels of effectiveness.

EXAMPLE 1

Spray compositions were prepared having excipient ingredients as shown in Table 1a. Lecithins used were sourced from Avanti. In addition to the excipient ingredients shown, all spray compositions contained glyphosate IPA salt. Three different glyphosate concentrations were used for each composition listed in Table 1a, selected to provide glyphosate a.e. rates as indicated in Table 1b.

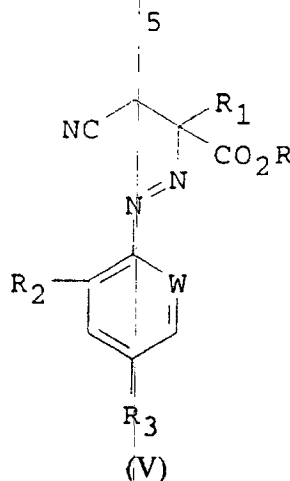
Compositions were prepared by the following procedure. The required amount of the selected lecithin, in powder form, was dispersed in 50 ml water by sonicating in a Fisher Sonic Dismembrator, Model 550, set at output level 8, for 3 minutes. The other ingredients, including glyphosate, were added after sonication. The pH of the spray composition was adjusted to 7 by addition of isopropylamine. The compositions were freshly prepared when applied in the greenhouse test of this Example.

Table 1a

Spray composition	Lecithin			% w/w
	g/l	phospho-lipid %	source	Fluorad FC-135
1-01	0.05	95	egg yolk	
1-02	0.02	95	egg yolk	
1-03	0.01	95	egg yolk	
1-04	0.05	95	soybean	
1-05	0.02	95	soybean	
1-06	0.01	95	soybean	
1-07	0.05	95	egg yolk	0.05
1-08	0.02	95	egg yolk	0.02
1-09	0.01	95	egg yolk	0.01
1-10	0.05	95	soybean	0.05
1-11	0.02	95	soybean	0.02
1-12	0.01	95	soybean	0.01

Velvetleaf (*Abutilon theophrasti*, ABUTH) and Japanese millet (*Echinochloa crus-galli*, ECHCF) plants were grown and treated by the standard procedures given above. Applications of spray compositions were made 16 days after planting ABUTH and 19 days after planting ECHCF, and evaluation of herbicidal inhibition was done 15 days after application.

As comparative treatments, Formulation B and Formulation C were applied alone and in tank-mix with Fluorad FC-135. Results, averaged for all replicates of each treatment, are shown in Table 1b.



wherein W, R, R₁, R₂ and R₃ are as defined above, followed by the cyclisation of said compound of formula (V).

Compounds of formula (V) above possess a chiral centre giving rise to different enantiomers, and also may exist as different geometric isomers or mixtures thereof. All such forms are embraced by the present invention. In this process, the product of reaction step (a) is generally acidified with an alcoholic solution of a mineral acid, preferably an ethanolic solution of hydrogen chloride. This also ensures that any acid by-product of the reaction step (a) (leading to the corresponding compound of formula (I) in which R is replaced by hydrogen) is re-esterified. For these reasons it is also preferred that in this process, reaction step (a) takes place under substantially anhydrous conditions.

Reaction step (b) is generally performed in the presence of an inert solvent, for example water, acetonitrile, dichloromethane or DMF, or more preferably an alcoholic solvent (e.g. methanol or ethanol) and is optionally buffered (e.g. with sodium acetate). The diazonium salt of a compound of formula (IV) may be prepared using diazotising agents known in the literature and is conveniently prepared with a molar equivalent of sodium nitrite and a mineral acid (e.g. hydrochloric or sulphuric acid), at a temperature of from about -10°C to about 50°C, more preferably from about 0°C to about 5°C. The diazonium salt of the compound of formula (IV) is generally prepared *in situ* as solvents such as alcohols tend to reduce diazonium salts quickly. In the present reaction, the reaction of the diazonium

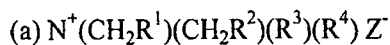
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WHAT IS CLAIMED IS:

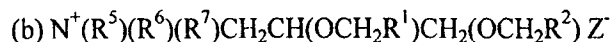
1. A plant treatment composition comprising (a) an exogenous chemical and (b) a first excipient substance which forms liposomes in aqueous dispersion and which consists of one or more compounds each having (i) a hydrophilic moiety comprising a cationic group and (ii) a hydrophobic moiety comprising two hydrocarbyl or acyl chains, wherein about 40 to 100 percent of said chains in the composition are saturated linear alkyl or alkanoyl groups having about 8 to about 22 carbon atoms.

2. The composition of claim 1 wherein about 40 to 100 percent of said chains in the composition are saturated linear alkyl or alkanoyl groups having about 12 to about 18 carbon atoms.

3. The composition of claim 1, wherein the first excipient substance comprises a liposome-forming compound having a hydrophobic moiety comprising two independently saturated or unsaturated hydrocarbyl groups R^1 and R^2 each independently having about 7 to about 21 carbon atoms, said liposome-forming compound having a formula selected from the group consisting of:



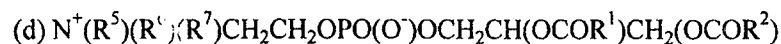
wherein R^3 and R^4 are independently hydrogen, C_{1-4} alkyl or C_{1-4} hydroxyalkyl and Z is a suitable anion;



wherein R^5 , R^6 and R^7 are independently hydrogen, C_{1-4} alkyl or C_{1-4} hydroxyalkyl and Z is a suitable anion;



wherein R^5 , R^6 , R^7 and Z are as defined above; and



wherein R^5 , R^6 , and R^7 are as defined above.

4. The composition of claim 3, wherein Z is selected from the group consisting of hydroxide, chloride, bromide, iodide, sulfate, phosphate and acetate.

5. The composition of claim 3, wherein R^1 and R^2 are independently saturated straight-chain alkyl groups each having about 7 to about 21 carbon atoms.

6. The composition of claim 3, wherein the first excipient substance is a phospholipid selected from the group consisting of di- C_{8-22} -alkanoylphosphatidylcholines and di- C_{8-22} -alkanoylphosphatidylethanolamines.

7. The composition of claim 6, wherein the first excipient substance is a dipalmitoyl or distearoyl ester of phosphatidylcholine or a mixture thereof.

8. The composition of claim 1 wherein the first excipient substance is a phospholipid or mixture of phospholipids selected from the group consisting of di- C_{8-22} -acylphosphatidylcholines and di- C_{8-22} -acylphosphatidylethanolamines, wherein about 40 to 100 percent of the acyl chains are saturated alkanoyl chains.

salt of the compound of formula (IV) to give a compound of formula (V) above generally occurs faster than the reduction of the diazonium salt.

Subsequent hydrolysis, preferably using mild conditions with a base such as aqueous sodium hydroxide, sodium carbonate or ammonia, may be necessary to effect the cyclisation of the compound of formula (V) to a compound of formula (III).

The molar ratio of the compounds of formula (II):(IV) is generally from about 1.5:1 to about 1:4, preferably from about 1.3:1 to about 1:1, more preferably about 1.1:1.

Compounds of formula (III) and (IV) above are described in the literature, for example see EP-A1-0295117. Compounds of formula (V) above are novel and thus constitute a further feature of the present invention.

The following non-limiting examples illustrate the invention.

Example 1

Preparation of ethyl 2,3-dicyanopropionate.

Potassium cyanide (13.0g, 0.2M) was stirred in absolute ethanol and ethyl cyanoacetate (22.6g, 0.2M) and paraformaldehyde (6.0g, 0.2m) were added at ambient temperature. After 5 minutes the white suspension was heated under reflux conditions for 12 minutes, and the orange solution was evaporated to dryness *in vacuo* at below 25°C to give a buff solid. The solid (the potassium salt) was dissolved in water (400ml), acidified to pH 5 with 2M hydrochloric acid solution, giving a red oil. This mixture was extracted with dichloromethane and the extracts dried and evaporated to dryness *in vacuo* to give the title compound as a red oil (23.5g), ¹H NMR (CDCl₃) δ 4.3 (2H, q), 3.95 (1H, t), 3.0 (2H, d), 1.35 (3H, t); identical with an authentic sample. Distilled material had b.p. 132-136°C at 0.5mmHg.

Yield : 77%.

Comparative example according to J. Chem. Soc. 89, 1460 (1906)

9. The composition of claim 1 wherein the first excipient substance is a phospholipid or mixture of phospholipids, about 40 to 100 percent of which consists of a dipalmitoyl or distearoyl ester of phosphatidylcholine or a mixture thereof.

10. The composition of claim 1 wherein the weight/weight ratio of the first excipient substance to the exogenous chemical is about 1:3 to about 1:100.

11. The composition of claim 1 wherein the first excipient substance is a lecithin of animal origin.

12. The composition of claim 11 wherein the lecithin is derived from egg yolk.

13. The composition of claim 1 wherein the exogenous chemical is a foliar-applied exogenous chemical.

14. The composition of claim 13 wherein the exogenous chemical is a pesticide, gametocide or plant growth regulator.

15. The composition of claim 14 wherein the exogenous chemical is a herbicide, nematocide or plant growth regulator.

16. The composition of claim 15 wherein the exogenous chemical is a herbicide.

17. The composition of claim 16 wherein the herbicide is selected from the group consisting of acetanilides, bipyridyls, cyclohexenones, dinitroanilines, diphenylethers, fatty acids, hydroxybenzonitriles, imidazolinones, phenoxies, phenoxypropionates, substituted ureas, sulfonylureas, thiocarbamates and triazines.

18. The composition of claim 16 wherein the herbicide is selected from the group consisting of acetochlor, alachlor, metolachlor, aminotriazole, asulam, bentazon, bialaphos, diquat, paraquat, bromacil, clethodim, sethoxydim, dicamba, diflufenican, pendimethalin, acifluorfen, C₉₋₁₀ fatty acids, fomesafen, oxyfluorfen, fosamine, flupoxam, glufosinate, glyphosate, bromoxynil, imazaquin, imazethapyr, isoxaben, norflurazon, 2,4-D, diclofop, fluazifop, quizalofop, picloram, propanil, fluometuron, isoproturon, chlorimuron, chlorsulfuron, halosulfuron, metsulfuron, primisulfuron, sulfometuron, sulfosulfuron, triallate, atrazine, metribuzin, triclopyr and herbicidal derivatives thereof.

19. The composition of claim 18 wherein the herbicide is glyphosate or a herbicidal derivative thereof.

20. The composition of claim 19 wherein the herbicide is glyphosate in its acid form.

21. The composition of claim 15 wherein the exogenous chemical is water-soluble.

22. The composition of claim 21 wherein the exogenous chemical is a salt having an anion portion and a cation portion.

23. The composition of claim 22 wherein at least one of said anion and cation portions is biologically active and has a molecular weight of less than about 300.

24. The composition of claim 23 wherein the exogenous chemical is paraquat or diquat.

25. The composition of claim 23 wherein the exogenous chemical exhibits systemic biological activity in the plant.

12 **EUROPEAN PATENT APPLICATION**

21 Application number: **86309981.8**

22 Date of filing: **19.12.86**

51 Int. Cl.4: **A01N 43/56**, A61K 31/415 ,
C07D 231/38 , A01N 55/00 ,
C07F 7/08 , C07D 231/44 ,
C07D 231/40 , C07D 231/18 ,
C07D 231/16 , C07D 231/14 ,
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30 Priority: **20.12.85 GB 8531485**

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54 **Pesticidal method using N-phenylpyrazoles.**

57 The invention provides a method for the control of arthropod, plant nematode or helminth pests using compounds of the formula:

EP 0 234 119 A1

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2005-09-20

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Señor:
Emilio Ferrero

Oficio N°

9603

REFERENCIA:	Radicación No.	00-29094.
	Trámite	002.
	Evento	001.
	Actuación	430.
	Folios	006.

Realizado el examen de patentabilidad de la presente solicitud según el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, **"art. 45.- Si la oficina nacional competente encontrara que la invención no es patentable o que no cumple con alguno de los requisitos establecidos en esta Decisión para la concesión de la patente, lo notificará al solicitante. Este deberá responder a la notificación dentro del plazo de sesenta días contados a partir de la fecha de la notificación. Este plazo podrá ser prorrogado por una sola vez por un período de treinta días adicionales.**

Cuando la oficina nacional competente estimara que ello es necesario para los fines del examen de patentabilidad, podrá notificar al solicitante dos o más veces conforme al párrafo precedente.

Si el solicitante no respondiera a la notificación dentro del plazo señalado, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, la oficina nacional competente denegará la patente." se notifica el siguiente Concepto Técnico:

1.DOCUMENTOS ESTUDIADOS

Para el presente estudio se tuvo en cuenta el capítulo descriptivo, folios 2 a 116, presentados originalmente y el capítulo reivindicatorio modificado como respuesta al requerimiento de forma (18 reivindicaciones), folios 289 a 299, donde las modificaciones se aceptaron dado que éstas no implican una ampliación de la solicitud originalmente presentada conforme lo establece el artículo 34 de la decisión 486 de la Comisión de la Comunidad Andina **"art. 34.- El solicitante de una patente podrá pedir que se modifique la solicitud en cualquier momento del trámite. La modificación no podrá implicar una ampliación de la protección que correspondería a la divulgación contenida en la solicitud inicial.**

Del mismo modo, se podrá pedir la corrección de cualquier error material."

- ❖ Se aceptó reivindicación de prioridad US60/130.756 del 23 de abril de 1999.

2.OBJETO DE LA INVENCION

Título: Método para mejorar la efectividad biológica de composiciones para el tratamiento de plantas conteniendo glifosato u otras sustancias químicas exógenas aniónicas.

- ❖ La invención consiste en un método para provocar la actividad biológica de una sustancia química exógena aplicada al follaje de una planta que comprende para la aplicación del tratamiento de dicho follaje una composición que contiene una sustancia química exógena aniónica caracterizado en que dicha aplicación se hace 6 horas antes de la lluvia o a la activación de la irrigación sobre la planta.
- ❖ El problema técnico expuesto en esta solicitud es proveer una alternativa útil a los métodos existentes para el mejoramiento de la actividad biológica de sustancias químicas exógenas aniónicas.
- ❖ La clasificación según la IPC correspondiente al objeto de la solicitud es A01N57/10.

3. CLARIDAD DE LA SOLICITUD

De acuerdo a la Decisión 486 de la Comisión de la Comunidad Andina en su Artículo 30.- *“Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción”*, en este sentido se anota que:

- El método de aplicación no se caracteriza por la composición que se aplica sino por la secuencia de etapas y condiciones especiales sobre las cuales se realice.
- De manera específica las reivindicaciones 2 a 6 no son claras porque se encabezan como método pero en realidad se definen o precisan características de cada uno de los componentes de la composición, la cual no es el objeto de la solicitud.
- Las reivindicaciones 17 y 18 son incoherentes porque no definen el método de aplicación sino la preparación de la composición que se aplica, es importante aclarar que la aplicación inédita o especial de una sustancia implica etapas y condiciones específicas pero de ninguna forma se refiere a las instrucciones generales que se aportan junto con el producto para que el usuario final las siga de forma convencional.
- Tampoco es claro que el método se caracterice por la aplicación de 6 horas antes de la lluvia (como se observa en la reivindicación principal número 1) ya que ésta es una variable que además depende de las condiciones meteorológicas y no del método como tal.

4. DETERMINACIÓN DEL ESTADO DE LATÉCNICA

- ❖ La fecha a partir de la cual se realizó la búsqueda de anterioridades corresponde al 22 de abril de 1999.
- ❖ Tomando como base lo anterior y la definición dada en el **art. 16.-** *“Una invención se considerará nueva cuando no está comprendida en el estado de la técnica.*

El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.

Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40.”, se realizó la búsqueda de anterioridades en los archivos con que cuenta esta Oficina y se encontraron los siguientes documentos relacionados con la materia de la presente solicitud:

N°	DOCUMENTO	TÍTULO	FECHA DE PUBLICACIÓN
D1	WO98/17109	Composition and method for treating plants with exogenous chemicals	1998-04-30
D2	WO98/17110	Composition and method for treating plants with exogenous chemicals	1998-04-30

6. EVALUACIÓN DE LOS REQUISITOS DE PATENTABILIDAD

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece que: *“Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial.”*

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

6.1 Evaluación del NIVEL INVENTIVO

De acuerdo al **art. 18.-** *"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica."*, se conceptúa:

La anterioridad D1 enseña métodos donde una sustancia química exógena es aplicada a las plantas para generar una respuesta biológica deseada. Ejemplos de sustancias químicas exógenas incluyen, pero no están limitadas por ellas, pesticidas químicos tales como herbicidas, algicidas, fungicidas, bactericidas, virucidas, insecticidas, aficidas, miticidas, nematocidas, molusquicidas y similares. Es ampliamente conocido que la asimilación de las composiciones pesticidas por las plantas se ve fuertemente influenciada por las condiciones ambientales tales como la temperatura, la humedad relativa, la presencia o ausencia de luz y por la salud de las plantas a ser tratadas. Como consecuencia de esta variabilidad, frecuentemente se administran cantidades muchos mayores de las que verdaderamente se necesitan donde la selección de las velocidades de aplicación se realizan de acuerdo a los conocimientos básicos de la persona medianamente versada en el arte correspondiente.

De esta manera la persona del oficio está en capacidad de reconocer, o de llegar hasta dicho conocimiento, las condiciones específicas de las plantas para lograr determinar las velocidades o dosis de aplicación efectivas. Existen muchos pesticidas que son ampliamente conocidos como es el caso del glifosato para el cual se tiene una gran información sobre las velocidades de aplicación apropiadas ya que con más de dos décadas de utilización de este pesticida se han publicado una enorme cantidad de estudios sobre las condiciones particulares requeridas para su administración.

D2 divulga, adicionalmente la aplicación de composiciones que contienen compuestos químicos exógenos para generar una respuesta biológica deseada a través de los medios convencionales como por ejemplo la atomización de líquidos y como modo de preferencia, se enseña la dilución de las composiciones concentradas.

En los ejemplos de D2 y D3 se muestra claramente las diversas recomendaciones y variables a controlar en el método de aplicación de este tipo de composiciones, de las cuales se consideran que corresponden a los normalmente reconocidos por una persona medianamente versada en la materia. Incluso se hace referencia al control en la irrigación, característica apenas obvia en una formulación que se realiza en el follaje ya que lógicamente bien sea por lluvias o por irrigación, el agua que cae sobre la planta desplaza la composición de tratamiento.

En cuanto al tiempo óptimo para rociar dependerá de la plaga, de los estados de desarrollo de las malezas y de las enfermedades. Como es de conocimiento básico el tiempo del tratamiento puede ser gobernado por las condiciones meteorológicas, las cuales pueden afectar las pérdidas por deriva y volatilidad de la aspersión. La temperatura, la humedad relativa, la dirección y la velocidad del viento y la lluvia, todas, pueden influir en la eficiencia del depósito del rociado. De esta forma, la persona del oficio a través de pruebas sistemáticas convencionales puede llegar a saber cuál es el tiempo que gasta la planta en asimilar un determinado pesticida (porque también depende de la estructura y composición química de la formulación aplicada) y con ello establecer de manera lógica las horas previas antes de irrigar la planta o si es posible hacer el cálculo (algo especulativo) para la aplicación antes de la lluvia. Evidentemente también la

persona del oficio podrá indicar las dosis para rellenar la aplicación si la aspersión original se diluye por lluvia inesperada poco después del rociado.

Como se puede observar, lo anterior demostraría contundentemente que ninguna de las características reclamadas en el método de la presente solicitud son especiales sino más bien resultan evidentes de la asociación del conocimiento de conjunto de la persona medianamente versada en el arte técnico con la materia revelada en las dos anterioridades citadas. En consecuencia, las reivindicaciones 1 a 18 carecerían de nivel inventivo.

En conclusión los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	DOCUMENTO	REIVINDICACIONES AFECTADAS	REQUISITO QUE AFECTA
D1	WO98/17109	1 a 18	NIVEL INVENTIVO
D2	WO98/17110	1 a 18	NIVEL INVENTIVO

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

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 CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

El anterior requerimiento fue notificado por fijación en lista, de fecha 20 OCT 2005

CONCEPTO TÉCNICO N° 1534(2005-09-07)	EXAMINADOR TÉCNICO CÓDIGO 202001	EXAMINADOR JURÍDICO CÓDIGO
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WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 25/30, 57/20, 25/08, 25/04		A1	(11) International Publication Number: WO 98/17109
			(43) International Publication Date: 30 April 1998 (30.04.98)
(21) International Application Number: PCT/US97/19329		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 24 October 1997 (24.10.97)		Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data: 60/029,317 25 October 1996 (25.10.96) US 60/034,887 31 January 1997 (31.01.97) US 60/039,789 4 March 1997 (04.03.97) US			
(71) Applicant: MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).			
(72) Inventors: GILLESPIE, Jane, L.; 7229 Cornell, St. Louis, MO 63130 (US). WARD, Anthony, J., I.; 821 Westwood Drive, Clayton, MO 63105 (US).			
(74) Agent: GOODMAN, Kenneth, D.; Arnold, White & Durkee, P.O. Box 4433, Houston, TX 77210 (US).			
(54) Title: COMPOSITION AND METHOD FOR TREATING PLANTS WITH EXOGENOUS CHEMICALS			
(57) Abstract			
Methods and compositions are disclosed wherein exogenous chemicals are applied to plants to generate a desired biological response. One embodiment of the present invention is a plant treatment composition that comprises (a) an exogenous chemical and (b) an alkylether surfactant or mixture of such surfactants having the formula $R^{12}-O-(CH_2CH_2O)_n(CH(CH_3)CH_2O)_m-R^{13}$ wherein R^{12} is an alkyl or alkenyl group having about 16 to about 22 carbon atoms, n is an average number of about 10 to about 100, m is an average number of 0 to about 5 and R^{13} is hydrogen or C_{1-4} alkyl. The alkylether surfactant or mixture thereof is present in an amount such that the weight/weight ratio of said alkylether surfactant or mixture of such surfactants to the exogenous chemical is about 1:3 to about 1:100.			

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WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 25/30, 57/20, 25/04, 25/28		A1	(11) International Publication Number: WO 98/17110
			(43) International Publication Date: 30 April 1998 (30.04.98)
(21) International Application Number: PCT/US97/19330		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
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(72) Inventor: WARD, Anthony, J., I.; 821 Westwood Drive, Clayton, MO 63105 (US).			
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(57) Abstract			
Methods and compositions are disclosed wherein exogenous chemicals are applied to plants to generate a desired biological response. One embodiment of the present invention is a plant treatment composition that comprises (a) an exogenous chemical and (b) a first excipient substance which forms liposomes in aqueous dispersion and which consists of one or more compounds each having (i) a hydrophilic moiety comprising a cationic group and (ii) a hydrophobic moiety comprising two hydrocarbyl or acyl chains, wherein about 40 to 100 percent of said chains in the composition are saturated linear alkyl or alkanoyl groups having about 8 to about 22 carbon atoms, preferably about 12 to about 18 carbon atoms.			