

SUPERINDUSTRIA Y COMERCIO
Radicación : 00017310 00000002
Fecha (AMD): 2000-05-25 15:18:52
Trámite : 002 PATENTES I 1 REGISTRO/ 329 COMPLEMEN
Dependencia: 2000 DIVISION DE NUEVAS CREACIONES

AA
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Señor

SUPERINTENDENTE DE INDUSTRIA Y COMERCIO

DIVISION DE NUEVAS CREACIONES

E. _____ S _____ D. _____

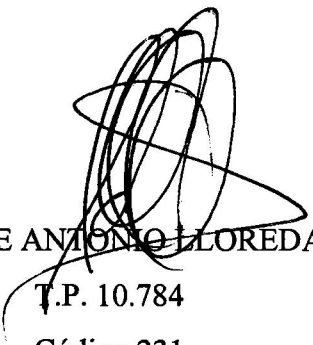
Re: P1.- AMERICAN CYANAMID COMPANY.- Solicitud de Patente de
Invencción para "COMPOSICIONES INSECTICIDAS SINERGICAS".-
Clase A01N.-Expediente número 00-017.310 .-

1. Me refiero a mi solicitud arriba nombrada de fecha 9 de Marzo de 2000.
2. Anexos me permito presentar a usted:
 - (1) Copias autenticas (2) de las primeras solicitudes de patente presentadas para el invento arriba nombrado **respecto de las cuales reclamo prioridad**, a saber:
 - (a) Copia autentica debidamente certificada de la solicitud estadinense número 60/124.306 de 12 de Marzo de 1999, junto con la traducción oficial No. 0243, correspondiente a las legalizaciones y reivindicaciones de dicho documento;
 - (b) Copia autentica debidamente certificada de la solicitud estadinense número 60/158.201 de 7 de Octubre de 1999, junto con la traducción oficial No.0244, correspondiente a las legalizaciones y reivindicaciones de dicho documento;
 - (2) Copia debidamente autenticada por el Notario Sexto del Circulo de Bogotá, de los documentos que acreditan la calidad de Traductor Oficial del señor Eduardo Calado Noguera quien elaboró la traducción de las solicitudes estadinenses números 60/124.306 y 60/158.201, respecto de las cuales se reivindica prioridad en el presente caso.

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- (3) Documento que acredita el traspaso que los autores del invento de la referencia hacen a favor de mi poderdante, de sus derechos sobre el mismo, debidamente legalizado hasta por el Ministerio de Relaciones Exteriores de Colombia bajo el número 161642 de 16 de Mayo de 2000; y
- (4) Traducción Oficial No. 093, debidamente legalizada hasta por el Ministerio de Relaciones Exteriores de Colombia bajo el número 163867 de 18 de Mayo de 2000, correspondiente a las legalizaciones de dicho documento de traspaso.
3. Ruego a usted tomar atenta nota de lo anterior y proceder de conformidad.

Señor Superintendente,



JOSE ANTONIO LLOREDA
T.P. 10.784
Código 231

EL SUSCRITO JEFE DEL AREA DE
LEGALIZACIONES DEL MINISTERIO DE
RELACIONES EXTERIORES

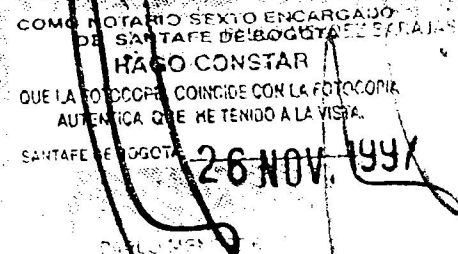
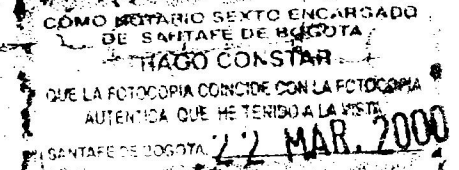
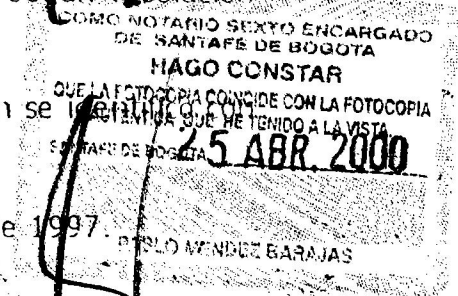
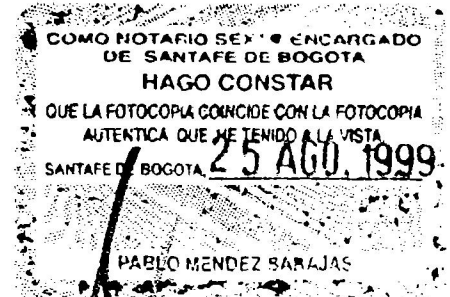
CERTIFICA

Que revisados los registros que se llevan en la oficina de Legalizaciones aparece la firma del señor **EDUARDO CALADO NOGUERA**, como traductor e intérprete oficial para los idiomas INGLES- ESPAÑOL, ESPAÑOL- INGLES, según resolución 541 del 27 de febrero de 1976.

La anterior certificación se expide a solicitud del interesado quien se cédula de ciudadanía 17.177.588 expedida en Bogotá.

Dada en Santa Fe de Bogotá, D.C., a los seis (6) de noviembre de 1997.

Blanca Acosta de García
BLANCA ACOSTA DE GARCIA
Jefe Area de Legalizaciones (e)



República de Colombia



Ministerio de Justicia y del Derecho

EL SECRETARIO GENERAL (E) DEL MINISTERIO DE
JUSTICIA Y DEL DERECHO

CERTIFICA:

Que por Resolución 541 del 27 de febrero de 1976, le fue expedida licencia para ejercer funciones de Traductor e Intérprete Oficial en los idiomas INGLÉS y ESPAÑOL al señor **EDUARDO CALADO NOGUERA**, identificado con la cédula de ciudadanía No. 17.177.588 expedida en Bogotá.

Que dicha Resolución se encuentra vigente en la fecha.

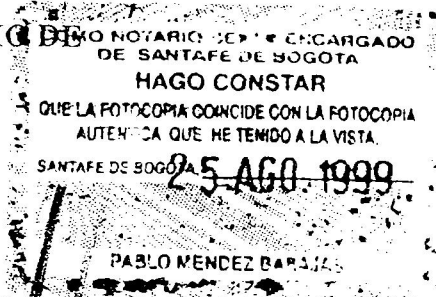
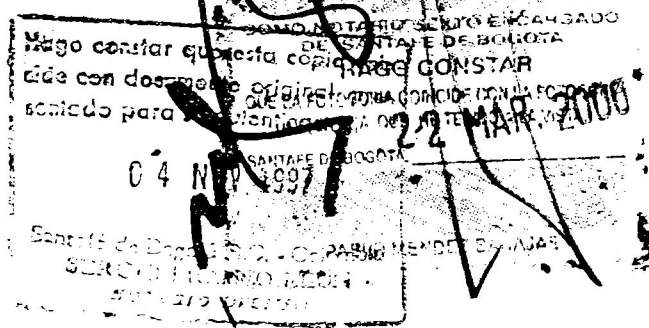
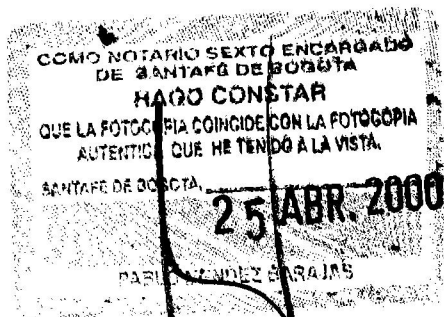
Se expide la presente certificación a solicitud del interesado.

Dada en Santa Fe de Bogotá, D.C., a

14 OCT. 1997

ALVARO NAMEN VARGAS

ICM/mmc



Abril 5, 2000
Traducción Oficial No.0243
REF: AMERICAN HOME PRODUCTS CORP
Patente No. 60/124,306

(American Cyanamid Company)
Caso-33,562-00

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DEPARTAMENTO DE COMERCIO DE LOS ESTADOS
UNIDOS
OFICINA DE MARCAS Y PATENTES

Marzo 28, 2000

Por medio del presente documento se certifica que adjunta se encuentra una fiel copia de los registros de la Oficina de Marcas y Patentes de los Estados Unidos, correspondientes a los documentos para la solicitud tal como se presentaron, con el fin de asignarle una fecha de registro bajo la norma del código 35 USC 111.

Número de Solicitud: 60/124,306

Fecha de Registro: Marzo 12, 1999

Autorizado por:

COMISIONADO DE MARCAS Y PATENTES

Firma: P. SWAIN

Funcionario Encargado de Certificaciones

Hay sello de la Oficina de Marcas y Patentes de color dorado.

Eduardo Calacal

Assistant Commissioner for Patents
Box Patent Application
Washington, D.C. 20231

Caso No:33562L

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SOLICITUD PROVISIONAL

Por medio de la presente se realizan los trámites necesarios para la solicitud de patente de los siguientes inventor(es).

Michael Frank Treacy, Paul E. Resner, Raymond Frank Borysewicz;
Hassan Oloumi, Kurt Allen Schwinghammer;
para el invento: COMPOSICIONES SINERGETICAS PARA
INSECTICIDAS

1. Se adjuntan Documentos requeridos para el registro bajo el código 37 CFR 1.51(a) (2) y 1.53(b) (2):
 - 17 páginas para especificación
 - 12 páginas de Reivindicaciones
 - 1 Página (s) de Resumen
 - Páginas de Gráficas
 - ☐ Formal
 - ☐ Informal
2. Nombres de inventor(es) y dirección (es) (o lista de abogados en el caso como identificador alfanumérico):

Michael Frank Treacy

Eduardo Caludosh

53 Sequoia Drive
Newtown, PA 18940

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Paul Resner
1267 Woodthrush Court
Yardley, PA 19067

Raymond Frank Borysewicz
12 Albermarle Road
Hamilton Square, NJ 08690

Kurt Allen Schwinghammer
1206 University Drive
Yardley, PA 19067

Hassan Oloumi
1204 Goldenrod Court
Yardley, PA

3. Traspaso

Un traspaso del invento a nombre de:

[] Fue realizada en la solicitud anterior y registrada como PTO
en _____, Carrete _____, Cuadro.

[] Se adjunta bajo Formulario de Registro por separado.

Eduardo Calado

[x] a continuación.

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CERTIFICADO DE ENVIO POSTAL BAJO CÓDIGO 37 CFR 1.10

Yo, por medio del presente documento certifico que este ha sido enviado por Servicio Postal del Correo de los Estados Unidos de América, en la fecha anteriormente mencionada en un sobre rotulado "Correo Postal al Destinatario" con número de envío: EM165269182 US, rotulado al Comisionado Asistente para Patentes, Box Patent Application, Washington, DC., 20231.

Firma: John W. Hogan Jr.

Fecha: Marzo 12, 1999

4. Registro de Honorarios \$150.00

5. Método de pago de Honorarios:

Cobrar a la cuenta corriente No 01-1300 por la suma de \$150.00

Eduardo Calado

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Se adjunta un duplicado del trámite.

6. Instrucciones en caso de que se registre un Sobre pago:
Acreditar cualquier sobre pago a la cuenta bancaria No. 01-1300.

7. Autorización para Cobros Adicionales de Honorarios

[x] El comisionado se encuentra autorizado para cobrar cualquier honorario adicional que se presente en este documento y durante la vigencia de esta solicitud a la Cuenta Corriente No. 01-1300:

[x] 37 CFR 1.51(a), (2) y 1.53 (c) registro de honorarios

[x] recargo para registro de honorarios básicos y/o primera página en una fecha posterior de la fecha registrada de esta solicitud.

8. Abogados/Nombres de representantes/No. de Registro

William H. Calnan	Reg No. 29,520
Charles F. Costello	Reg No. 27, 324
Gregory M. Hill	Reg No. 31,369
John W. Hogan, Jr.	Reg No. 32,703
Joseph M. Mazzaresse	Reg No. 32,803
Barbara L. Renda	Reg No. 27, 626

Edward Caludo

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9. Dirección para correspondencia

John W. Hogan, Jr.

American Home Products Corporation

Patent Law Department

One Campus Drive

Parsippany, NJ 07054

Tel: (973) 683-2152

10. El invento fue realizado por una agencia del Gobierno de los Estados Unidos o bajo Contrato con una agencia del Gobierno de los Estados Unidos.

☒ No

☐ Si, el nombre de dicha Agencia del Gobierno de los Estados Unidos y número de contrato son los siguientes:

Firma: John W. Hogan Jr.

No de Registro: 32,703

American Home Products Corporation

Patent Law Department

One Campus Drive

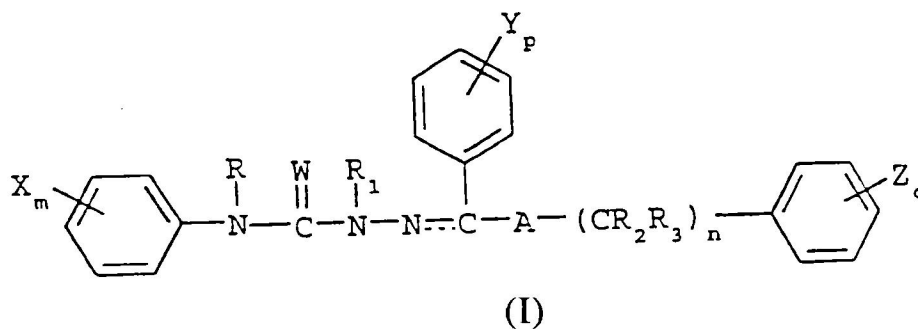
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Tels. No. (973) 683-2152

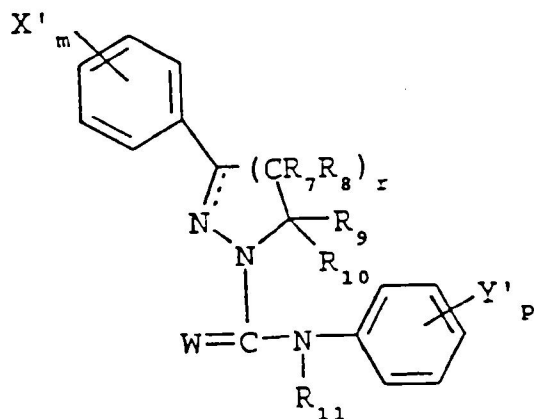
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REIVINDICACIONES :

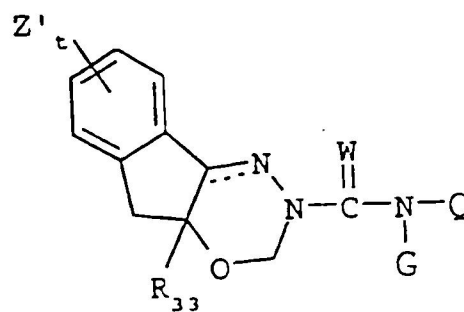
1. Una composición sinérgica insecticida la cual consta de una cantidad sinérgicamente eficaz de un canal de sodio neuronal antagonista mezclado con uno o más compuestos seleccionados del grupo A.
2. La composición de acuerdo a la reivindicación 1 la cual tiene un compuesto de un canal neuronal de sodio antagonista de la formula



Edwards Walsh



(II)



(III)

en el cual A es CR₄R₅ o NR₆;

W es O o S;

X, Y, Z, X', Y', y Z' son cada uno independientemente H;

halógeno; OH; CN; NO₂; C₁-C₆- alquilo opcionalmente

sustituido con uno o más halógenos, C₁-C₃ alcoxi, C₁-C₃

haloalcoxi, C₃-C₆ cicloalquilo, C₂-C₆ alquenilo o grupos

de sulfonilo;

C₁-C₆ alcoxi opcionalmente sustituidos con uno o más halógenos,

C₁-C₃-alcoxi o C₃-C₆ grupos de cicloalquilo;

Edwardo Celada

C1-C6 alcoxycarbonilo, C3-C6 cicloalquilocarbonilo, fenilo
opcionalmente sustituido con uno o más halógenos, C1-C4 alquilo o
C1-C4 grupos de alcoxi;

aminocarbonilo opcionalmente sustituido por uno o más grupos de
C1-C3- alquilo;

C1-C6 alcoxycarbonilo; C1-C6 alquilosulfonilo;
C2-C6 alqueno; o NR₁₂R₁₃;

m, p y q son cada uno un número entero de 1, 2, 3, 4, o 5;

n es un número entero de 0, 1 o 2;

r es un número entero de 1 hasta 2;

t es un número entero de 1, 2, 3, o 4;

R, R₁, R₂, R₃, R₄ y R₅ son cada uno independientes de H o C1-C4
alquilo;

R₆ es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C6 alcoxialquilo, C1-
C6 alcoxi, C1-C6 haloalcoxi, C2-C6 alqueno, C2-C6 alqueno, C2-
C6 alquino, C1-C6 alquilocarbonilo, C1-C6 alcoxycarbonilo, C1-C6
alquiltio, o C1-C6 haloalquiltio;

Eduardo Delgado

R7 y R8 son cada uno independientes de H; halógeno; C1-C6alquilo; C1-C6 alquilocarboniloxi; o fenilo opcionalmente sustituido con uno o más halógenos, CN, NO₂, C1-C6alquilo, C2-C6 haloalquilo, C1-C6alcoxi o C1-C6 grupos de haloalcoxi;

R9 y R10 son cada uno independientes de H, o C1-C4alquilo; R11 es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C4 alquilocarbonilo, C1-C6 alcoxicarbonilo o C1-C6 haloalcoxycarbonilo;

R12 y R13 son cada uno independientes de H o C1-C6 alquilo; G es H; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, C1-C4 alcoxi, C1-C6haloalcoxi, CN, NO₂S (O)uR14, COR15, CO₂R16, fenilo o C3-C6 grupos de cicloalquilo;

C1-C6alcoxi; C1-C6 haloalcoxi; CN; NO₂; S(O)u R17; COR18; CO₂R19; fenilo opcionalmente sustituido con uno o más halógenos, CN, C1-C3 haloalquilo o C1-C3 grupos de haloalquilo;

C3-C6 cicloalquilo; Feniltio;

Edwards Calasch

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Q es fenilo opcionalmente sustituido con uno o más halógenos, CN, SCN, NO₂, S(O)_uR₂₀, C1-C4 alquilo, C1-C4-haloalquilo, C1-C4 alcoxialquilo, C1-C6 alcoxi, C1-C6haloalcoxi, o grupos de NR₂₁R₂₂;

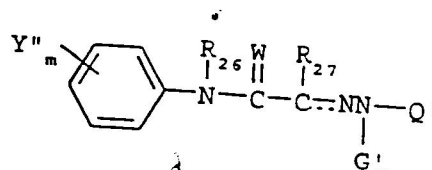
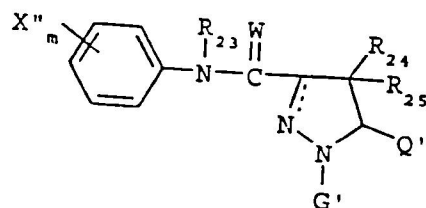
R₁₄, R₁₅, R₁₆, R₁₈, R₁₉, R₂₁ y R₂₂ son cada uno independientes de H o C1-C6 alquilo;

R₁₇ y R₂₀ son cada uno independientes de C1-C6 alquilo o C1-C6 haloalquilo;

R₃₃ es CO₂R₃₄;

R₃₄ es H, C1-C6 alquilo, C1-C6 haloalquilo, fenilo o halofenilo; y la configuración de la línea de puntos C...N representa un doble enlace o un enlace único; o un estereoisómero del mismo.

3. La composición de acuerdo a la reivindicación 1 la cual tiene un compuesto de un canal neuronal de sodio antagonista de la formula:



Charles Palacios

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(IV)

(V)

en el cual W es O u S;

X' y Y' son independientes de H; halógeno; CN; SCN; C1-C6 alquilo
opcionalmente sustituido con uno o más halógenos, NO₂, CN, C1-C4
alcoxi, C1-C4 alquiltio, fenilo, halofenilo, C1-C4 alquilosulfonilo,
C1-C4 haloalquilosulfonilo o C1-C4 grupos de alcoxycarbonilo;

C2-C4 alquenilo, C2-C4 haloalquenilo, C2-C4 alquinilo; C2-C4
haloalquinilo; C3-C6 cicloalquilo; C3-C6 halocicloalquilo; fenilo
opcionalmente sustituido con uno o mas halógenos, CN, NO₂, C1-C4
alquilo, C1-C4 haloalquilo, C1-C4alcoxi, C1-C4 haloalcoxi, C1-C4
alquiltio, C1-C4 alquilosulfonilo o grupos de C1-C4
haloalquilosulfonilo;

C1- C4 alquilocarbonilo; C1-C4 haloalquilocarbonilo; o NR_{28R29};

m es un número entero de 1, 2, 3, 4, o 5;

G' es fenilo opcionalmente sustituido con uno o más grupos los
cuales pueden ser iguales o diferentes seleccionados de X' ;

Edwards

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un anillo heteroaromatico de 5 miembros que contiene de uno a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1 azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo heteroaromatico de 5 miembros el cual se encuentra unido por medio del carbono y este puede ser opcionalmente sustituido con uno o más grupos, los cuales pueden ser iguales o diferentes, seleccionados de X'; o

un anillo heteroaromatico de 6 miembros que contiene de uno a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1 azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo heteroaromatico de 6 miembros el cual se encuentra unido por medio del carbono y este puede ser opcionalmente sustituido con uno o más grupos, los cuales pueden ser iguales o diferentes, seleccionados de X';

Q es H; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, CN, C1-C3 alcoxi, C1-C6 alcoxycarbonilo o fenilo opcionalmente sustituido con uno o más halógenos, CN, NO₂, C1-C4 alquilo, C1-C4 haloalquilo, C1-C4 alquilosulfonilo o grupos de C1-C4 alquilosulfinilo;

Eduardo Calado

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C2- C6 alquenilo; C2-C6 alquinilo; o fenilo opcionalmente sustituido con uno o hasta tres grupos, los cuales pueden ser iguales o diferentes, seleccionados de X' ;

R23, R24, R25, R26, R27, R28 y R29 son cada uno independientes de H o C1-C4 alquilo; y la configuración de la línea de puntos C.-.N representa un enlace doble o un enlace sencillo; o un estereoisómero del mismo.

4. La composición de acuerdo a la reivindicación 2 en la cual el canal neuronal de sodio antagonista es un compuesto de acuerdo a la formula I o III.
5. La composición de acuerdo a la reivindicación 4 en la cual la configuración de la línea de puntos C.-.N representa un doble enlace.
6. La composición de acuerdo a la reivindicación 5 en la cual el compuesto de la formula III se encuentra en la forma S.
7. La composición de acuerdo a la reivindicación 6 en la cual

Eduardo Calado

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W es O; X es trifluorometoxi y se encuentra en la 4 posición; Y es trifluorometoxi y se encuentra en la 3 -posición; Z es CN y se encuentra en la 4-posición; A es CH₂; n es 0; m, p y q son cada uno independientes de 1; R y R₁ son cada uno independientes de H; Z' es Cl; R₃₃ y G son cada uno independientes de CO₂CH₃; y Q es p-(trifluorometoxi) fenilo.

8. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del grupo A son cipermetrina, cihalometrina, ciflutrin, permetrin, etofenprox o silafluofen.

9. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del Grupo A son profenofos, acefato, sulprofos, malation, diazinon, metilo paration o terbufos.

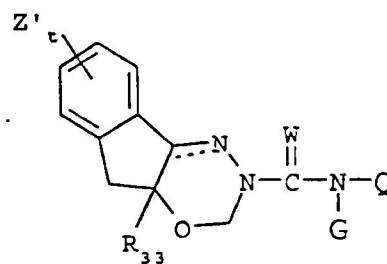
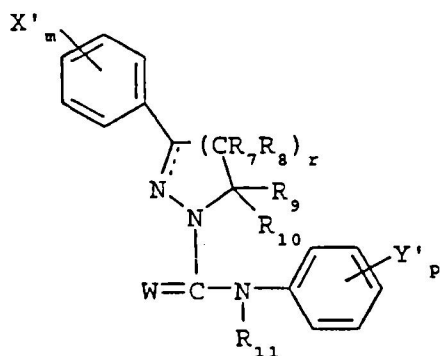
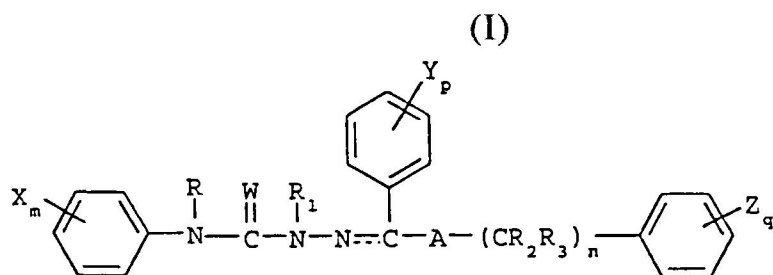
10. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del grupo A son metonilo, tiodicarbo o fenotiocarbo.

11. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del grupo A son amitraz, *Calvario Calvario* - clorodimeform o clorofenamidina.

12. La composición de acuerdo a la reivindicación 7 en la cual el o los compuestos seleccionados del grupo A son avermectina, anamectina, milbemectina, nemadectina, o moxidectina.
13. La composición de acuerdo a la reivindicación 7 en la cual el o los compuestos seleccionados del grupo A son hidrametilnon.
14. La composición de acuerdo a la reivindicación 7 en la cual el o los compuestos seleccionados del grupo A son fipronil, endosulfon, imidacloprid, acetamiprid, nitenpiram o tiametoxam.
15. Un método para el control sinérgico de insectos el cual consiste en hacer contacto con dicho insecto con una cantidad sinérgicamente eficaz de un canal neuronal de sodio antagonista combinado con uno o más compuestos seleccionados del grupo A.
16. El método de acuerdo a reivindicación 15 el cual tiene un compuesto de un canal neuronal de sodio antagonista de la fórmula:

Eduardo Calado

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en el cual A es CR₄R₅ o NR₆;

W es O o S;

X, Y, Z, X', Y', y Z' son cada uno independientemente H;

halógeno; OH; CN; NO₂; C₁-C₆- alquilo opcionalmente

sustituido con uno o más halógenos , C₁-C₃ alcoxi, C₁-C₃

haloalcoxi, C₃-C₆ cicloalquilo, C₂-C₆ alqueniloxi o grupos

de sulfoniloxi;

Edwardo Alarín

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C1-C6 alcoxi opcionalmente sustituidos con uno o más halógenos,

C1-C3-alcoxi o C3-C6 grupos de cicloalquilo;

C1-C6 alcoxycarbonilo, C3-C6 cicloalquilocarboniloxi, fenilo

opcionalmente sustituido con uno o más halógenos, C1-C4 alquilo o

C1-C4 grupos de alcoxi;

aminocarboniloxi opcionalmente sustituido por uno o más grupos de

C1-C3- alquilo;

C1-C6 alcoxycarboniloxi; C1-C6 alquilosulfoniloxi;

C2-C6 alquenilo; o NR₁₂R₁₃;

m, p y q son cada uno un número entero de 1, 2, 3, 4, o 5;

n es un número entero de 0, 1 o 2;

r es un número entero de 1 hasta 2;

t es un número entero de 1, 2, 3, o 4;

R, R₁, R₂, R₃, R₄ y R₅ son cada uno independientes de H o C1-C4

alquilo;

Eduardo Calado

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R6 es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C6 alcoxialquilo, C1-C6 alcoxi, C1-C6 haloalcoxi, C2-C6 alquenilo, C2-C6 alquenilo, C2-C6 alquinilo, C1-C6 alquilocarbonilo, C1-C6 alcoxycarbonilo, C1-C6 alquiltio, o C1-C6 haloalquiltio;

R7 y R8 son cada uno independientes de H; halógeno; C1-C6alquilo; C1-C6 alquilocarbonilo; o fenilo opcionalmente sustituido con uno o más halógenos, CN, NO₂, C1-C6alquilo, C2-C6 haloalquilo, C1-C6alcoxi o C1-C6 grupos de haloalcoxi;

R9 y R10 son cada uno independientes de H, o C1-C4alquilo;

R11 es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C4 alquilocarbonilo, C1-C6 alcoxycarbonilo o C1-C6 haloalcoxycarbonilo;

R12 y R13 son cada uno independientes de H o C1-C6 alquilo;

G es H; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, C1-C4 alcoxi, C1-C6haloalcoxi, CN, NO₂S (O)uR14, COR15, CO₂R16, fenilo o C3-C6 grupos de cicloalquilo;

Edwards Calado R.

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C1-C6alcoxi; C1-C6 haloalcoxi; CN; NO₂; S(O)_u R17; COR18;
CO₂R19; fenilo opcionalmente sustituido con uno o más halógenos,
CN, C1-C3 haloalquilo o C1-C3 grupos de haloalquilo;

C3-C6 cicloalquilo; Feniltio;

Q es fenilo opcionalmente sustituido con uno o más halógenos, CN,
SCN, NO₂, S(O)_uR20, C1-C4 alquilo, C1-C4-haloalquilo, C1-C4
alcoxialquilo, C1-C6 alcoxi, C1-C6haloalcoxi, o grupos de
NR21R22;

R14, R15, R16, R18, R19, R21 y R22 son cada uno independientes
de H o C1-C6 alquilo;

R17 y R20 son cada uno independientes de C1-C6 alquilo o C1-C6
haloalquilo;

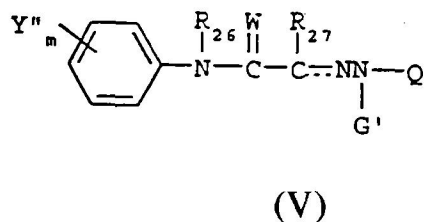
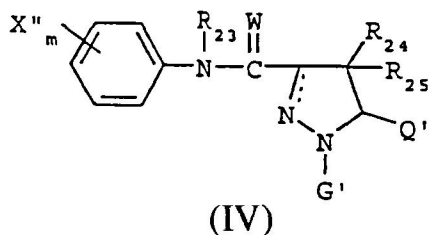
R33 es CO₂R34;

R34 es H, C1-C6 alquilo, C1-C6 haloalquilo, fenilo o halofenilo; y la
configuración de la línea de puntos C-.N representa un doble enlace
o un enlace único; o un estereoisómero del mismo.

Edwards Celso A.

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17. Un método de acuerdo a la reivindicación 15 la cual tiene un compuesto de un canal de sodio antagonista de la formula:



en el cual W es O u S;

X' y Y' son independientes de H; halógeno; CN; SCN; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, NO₂, CN, C1-C4 alcoxi, C1-C4 alquiltio, fenilo, halofenilo, C1-C4 alquilosulfonilo, C1-C4 haloalquilosulfonilo o C1-C4 grupos de alcoxycarbonilo;

C2-C4 alquenilo, C2-C4 haloalquenilo, C2-C4 alquinilo; C2-C4 haloalquinilo; C3-C6 cicloalquilo; C3-C6 halocicloalquilo; fenilo opcionalmente sustituido con uno o mas halógenos, CN, NO₂, C1-C4 alquilo, C1-C4 haloalquilo, C1-C4alcoxi, C1-C4 haloalcoxi, C1-C4 alquiltio, C1-C4 alquilosulfonilo o grupos de C1-C4 haloalquilosulfonilo;

C1- C4 alquilocarbonilo; C1-C4 haloalquilocarbonilo; o NR₂₈R₂₉;

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m es un número entero de 1, 2, 3, 4, o 5;

G' es fenilo opcionalmente sustituido con uno o más grupos los cuales pueden ser iguales o diferentes seleccionados de X' ;

un anillo heteroaromatico de 5 miembros que contiene de uno a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1 azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo heteroaromatico de 5 miembros el cual se encuentra unido por medio del carbono y este puede ser opcionalmente sustituido con uno o más grupos, los cuales pueden ser iguales o diferentes, seleccionados de X'; o

un anillo heteroaromatico de 6 miembros que contiene de uno a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1 azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo heteroaromatico de 6 miembros el cual se encuentra unido por medio del carbono y este puede ser opcionalmente sustituido con uno o más grupos, los cuales pueden ser iguales o diferentes, seleccionados de X';

Edwards Calado

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Q es H; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, CN, C1-C3 alcoxi, C1-C6 alcoxycarbonilo o fenilo opcionalmente sustituido con uno o más halógenos, CN, NO₂, C1-C4 alquilo, C1-C4 haloalquilo, C1-C4 alquilosulfonilo o grupos de C1-C4 alquilosulfinilo;

C2- C6 alquenilo; C2-C6 alquinilo; o fenilo opcionalmente sustituido con uno o hasta tres grupos, los cuales pueden ser iguales o diferentes, seleccionados de X' ;

R23, R24, R25, R26, R27, R28 y R29 son cada uno independientes de H o C1-C4 alquilo; y la configuración de la línea de puntos C.-.N representa un enlace doble o un enlace sencillo; o un estereoisómero del mismo.

18. El método de acuerdo a la reivindicación 16 en la cual el canal neuronal de sodio antagonista es un compuesto de la formula I o III.

19. El método de acuerdo a la reivindicación 18 en la cual la configuración de la linea de puntos representa un doble enlace.

Edwars Carlos

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20. Un método de acuerdo a la reivindicación 19 en la cual la formula III del compuesto se encuentra en la forma S.

21. El método de acuerdo a la reivindicación 20 en la cual W es O; X es trifluorometoxi y se encuentra en la 4 posición; Y es trifluorometoxi y se encuentra en la 3 -posición; Z es CN y se encuentra en la 4-posición; A es CH₂; n es 0; m, p y q son cada uno independientes de 1; R y R₁ son cada uno independientes de H; Z' es Cl; R₃₃ y G son cada uno independientes de CO₂CH₃; y Q es p-(trifluorometoxi) fenilo.

22. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del grupo A son cipermetrina, cihalometrina, ciflutrin, permetrin, etofenprox o silafluofen.

23. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del Grupo A son profenofos, acefato, sulprofos, malation, diazinon, metilo paration o terbufos.

Eduardo Colado

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24. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del grupo A son metonilo, tiodicarbo o fenotiocarbo.

25. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del grupo A son amitraz, clorodimeform o clorofenamidina.

26. La composición de acuerdo a la reivindicación 21 en la cual el o los compuestos seleccionados del grupo A son avermectina, anamectina, milbemectina, nemadectina, o moxidectina.

27. La composición de acuerdo a la reivindicación 21 en la cual el o los compuestos seleccionados del grupo A son hidrametilnon.

28. La composición de acuerdo a la reivindicación 21 en la cual el o los compuestos seleccionados del grupo A son fipronil, endosulfon, imidacloprid, acetamiprid, nitenpiram o tiametoxam.

29. Un método para proteger las plantas de ataques de insectos la cual consiste en aplicar al follaje de dicha planta una cantidad

Edvardo Calado

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sinérgicamente eficaz de la composición de acuerdo a la reivindicación 1.

30. El método de acuerdo a la reivindicación 29 en la cual los insectos son lepidoptera o coleoptera.

Eduardo Caludo

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THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

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March 28, 2000

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THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111.**

APPLICATION NUMBER: 60/124,306 ✓

FILING DATE: March 12, 1999



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

P. SWAIN

Certifying Officer

03/12/99
JCS98 U.S. PTO

Docket No: 33562L
Patent

APPROV. 75
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Assistant Commissioner for Patents
Washington, D.C. 20231

PROVISIONAL APPLICATION COVER SHEET

Transmitted herewith for filing under 37 CFR 1.53(c) is the provisional patent application of the following Inventor(s): Michael Frank Treacy, Paul E. Rensner, Raymond Frank Borysewicz, Hassan Oloumi, Kurt Allen Schwinghammer;
For: SYNERGISTIC INSECTICIDAL COMPOSITIONS;

JCS41 U.S. PTO
60/124306
03/12/99

1. Papers enclosed which are required for filing date under 37 CFR 1.51(a) (2) and 1.53 (b) (2):
- 17 Pages of specification
 - 12 Pages of claims
 - 1 Page(s) of abstract
 - Sheets of drawing
 - ☐ Formal
 - ☐ Informal

2. Inventor(s) name(s) and address(es) (or list attorney docket number as alphanumeric identifier):

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Raymond Frank Borysewicz 12 Abemarie Road Hamilton Square, NJ	Hassan Oloumi 1204 Goldenrod Court Yardley, PA
Kurt Allen Schwinghammer 1206 University Drive Yardley, PA 19067	

3. Assignment
An assignment of the invention:

- ☐ was made in the prior application and recorded in PTO on , Reel , Frame .
- ☐ is attached under separate Recordation Form Cover Sheet.
- ☒ will follow.

CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that this paper and the documents referred to as enclosed therein are being deposited with the United States Postal Service on the date written below in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EM165269182US addressed to the Assistant Commissioner for Patents, Box Provisional Patent Application, Washington, D.C. 20231.

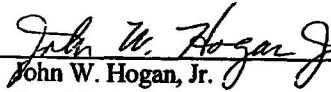
March 12, 1999
Date

John W. Hogan, Jr.
John W. Hogan, Jr.

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4. Filing Fee \$150.00
5. Method of Payment of Fees:
Charge Deposit Account No. 01-1300 in the amount of \$ 150.00
A duplicate of this transmittal is attached.
6. Instructions as to Overpayment:
Credit any overpayment to Deposit Account No. 01-1300.
7. Authorization to Charge Additional Fees
 - ☒ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Deposit Account No. 01-1300:
 - ☒ 37 CFR 1.51(a)(2) and 1.53 (c) filing fees
 - ☒ Surcharge for filing the basic filing fee and/or complete cover sheet on a date later than the filing date of the application.
8. Attorney/Agent Names/Registration Nos.

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10. The invention was made by an agency of the U.S. Government or under a contract with an agency of the U.S. Government.
 - ☒ No
 - ☐ Yes, the name of the U.S. Government agency and the Government contract numbers are ____.


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SYNERGISTIC INSECTICIDAL COMPOSITIONS

ABSTRACT OF THE INVENTION

The present invention provides a synergistic insecticidal composition comprising as essential active ingredients a neuronal sodium channel antagonist in combination with one or more compounds selected from the group consisting of pyrethroids, pyrethroid-type compounds, organophosphates, carbamates, formamidines, macrocyclic lactones, amidinohydrazones, GABA antagonists and acetylcholine receptor ligands.

Also provided are methods for synergistic insect control and crop protection.

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SYNERGISTIC INSECTICIDAL COMPOSITIONS

BACKGROUND OF THE INVENTION

Insecticidal agents and compositions have been developed to control insect pests such as agrohorticultural pests, hygienic pests, or wood-eating pests and in practice have been used as a single or a
5 mixed agent. However, economically efficient and ecologically safe insect control compositions are still being sought. Insecticidal compositions which allow for reduced effective dosage rates, increased environmental safety and lower incidence of insect resistance are
10 highly desirable. Although the rotational application of insect control agents having different modes of action may be adopted for good pest management practice, this approach does not necessarily give satisfactory insect control. Further, eventhough combinations of insect
15 control agents have been studied, a high synergistic action has not always been found. Obtaining an insecticidal composition which demonstrates no cross-resistance to existing insecticidal agents, no toxicity problems and little negative impact on the environment is
20 extremely difficult.

Therefore, it is an object of this invention to provide a synergistic insecticidal composition which demonstrates a high controlling effect with concomittant reduced crop production cost and reduced environmental load.

25 It is another object of this invention to provide methods for synergistic insect control and enhanced crop protection.

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SUMMARY OF THE INVENTION

The present invention provides a synergistic insecticidal composition comprising as essential active ingredients a synergistically effective amount of a neuronal sodium channel antagonist in combination with one or more compounds selected from the group consisting of pyrethroids, pyrethroid-type compounds, organophosphates, carbamates, formamidines, macrocyclic lactones, amidinohydrazones, GABA (gamma-aminobutyric acid) antagonists, and acetylcholine receptor ligands.

The present invention also provides a method for synergistic insect control which comprises contacting said insect with a synergistically effective amount of a neuronal sodium channel antagonist in combination with one or more compounds selected from the group consisting of pyrethroids, pyrethroid-type compounds, organophosphates, carbamates, formamidines, macrocyclic lactones, amidinohydrazones, GABA antagonists and acetylcholine receptor ligands.

The present invention further provides a method for the enhanced protection of plants from infestation and attack by insects.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

"Acetylcholine receptor ligand compound" as used in this application means a compound which is capable of binding to the acetylcholine receptor site.

"Group A" as used in this application means insecticidal

- 1) pyrethroid compounds;
- 2) pyrethroid-type compounds;
- 3) organophosphate compounds;
- 4) carbamate compounds;

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- 5) formamidine compounds;
- 6) macrocyclic lactone compounds;
- 7) amidinohydrazone compounds;
- 8) GABA antagonist compounds; and
- 5 9) acetylcholine receptor ligand compounds.

"Haloalkyl" as used in this application means an alkyl group C_xH_{2x+1} having 1 to $2x+1$ halogen atoms which may be the same or different. Similarly, the terms "haloalkenyl", "haloalkynyl", "haloalkoxy", "halophenyl" and the like mean mono- to perhalogen substitution
10 wherein the halogens may be the same or different.

"Halogen" as used in this application means Cl, Br, I or F.

"Neuronal sodium channel antagonist" as used in this
15 application means a compound which is capable of preventing the ability of a neuron cell to transfer sodium ions across the cell membrane.

"Pyrethroid-type compounds" as used in this application means those compounds characterized by a non-
20 ester linked aryl-phenoxybenzyl moiety.

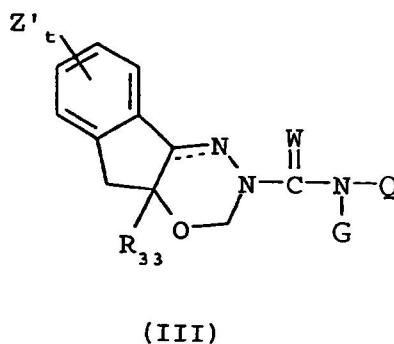
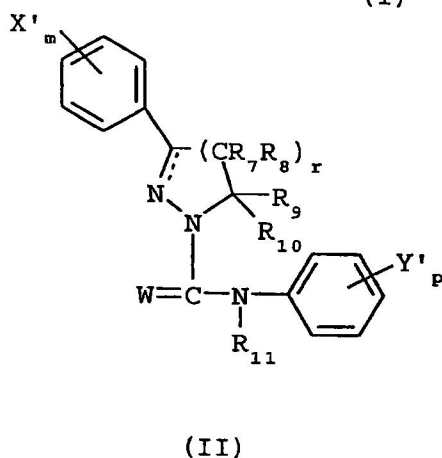
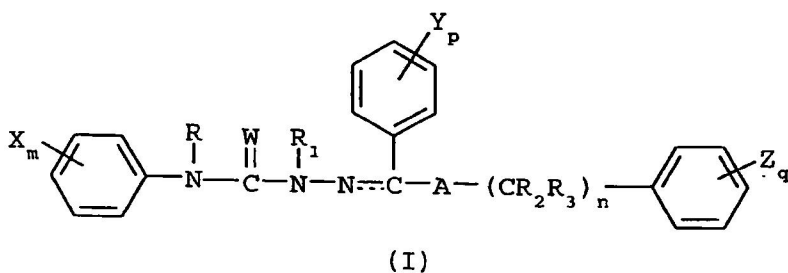
"Synergism" as used in this application means a cooperative action encountered in a combination of two or more biologically active components in which the combined activity of the two or more components exceeds the sum of
25 the activity of each component alone.

Surprisingly, it has now been found that a composition which comprises a combination of a neuronal sodium channel antagonist and a second insecticidal
30 ingredient provides superior insect control at lower levels of the combined active agents than may be achieved when the neuronal sodium channel antagonist or the second insecticidal ingredient is applied alone.

As previously stated, the term neuronal sodium
35 channel antagonist designates a compound which is capable

of preventing the ability of a neuron cell to transfer sodium ions across the cell membrane. A neuron cell thus affected is unable to fire, resulting in paralysis, and ultimately mortality, in the target host. Descriptions of neuronal sodium channel antagonists and their mode of action may be found in Pesticide Biochemistry and Physiology, 60: 177-185 or Archives of Insect Biochemistry and Physiology, 37: 91-103.

Neuronal sodium channel antagonists include compounds such as those described in U.S. 5,543,573; U.S. 5,708,170; U.S. 5,324,837 and U.S. 5,462,938, among other publications. Exemplary of the neuronal sodium channel antagonist compounds useful in the composition of this invention are those compounds having the structural formula



wherein A is CR_4R_5 or NR_6 ;
W is O or S;

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X, Y, Z, X', Y' and Z' are each independently H;
halogen; OH; CN; NO₂; C₁-C₆alkyl optionally
substituted with one or more halogen, C₁-
C₃alkoxy, C₁-C₃haloalkoxy, C₃-C₆cycloalkyl,
5 C₂-C₆alkenyloxy or sulfonyloxy groups;
C₁-C₆alkoxy optionally substituted with one or
more halogen, C₁-C₃alkoxy or C₃-C₆cycloalkyl
groups;
C₁-C₆alkoxycarbonyl, C₃-C₆cycloalkylcarbonyloxy,
10 phenyl optionally substituted with one or
more halogen, C₁-C₄alkyl, or C₁-C₄alkoxy
groups;
aminocarbonyloxy optionally substituted with
one or more C₁-C₃alkyl groups;
15 C₁-C₆alkoxycarbonyloxy; C₁-C₆alkylsulfonyloxy;
C₂-C₆alkenyl; or NR₁₂R₁₃;
m, p and q are each independently an integer of 1,
2, 3, 4, or 5;
n is an integer of 0, 1 or 2;
20 r is an integer of 1 or 2;
t is an integer of 1, 2, 3 or 4;
R, R₁, R₂, R₃, R₄ and R₅ are each independently H or
C₁-C₄alkyl;
R₆ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxyalkyl,
25 C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyl, C₂-
C₆alkynyl, C₁-C₆alkylcarbonyl, C₁-C₆alkoxy-
carbonyl, C₁-C₆alkylthio, or C₁-C₆haloalkylthio;
R₇ and R₈ are each independently H; halogen; C₁-
C₆alkyl; C₁-C₆alkylcarbonyloxy; or phenyl
30 optionally substituted with one or more
halogen, CN, NO₂, C₁-C₆alkyl, C₂-C₆halo-
alkyl, C₁-C₆alkoxy or C₁-C₆haloalkoxy
groups;
R₉ and R₁₀ are each independently H, or C₁-C₄alkyl;
35 R₁₁ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-

C₄alkylcarbonyl, C₁-C₆alkoxycarbonyl, or C₁-C₆haloalkoxycarbonyl;

R₁₂ and R₁₃ are each independently H or C₁-C₆alkyl;

G is H; C₁-C₆alkyl optionally substituted with one or
5 more halogen, C₁-C₄alkoxy, C₁-C₆haloalkoxy, CN, NO₂S(O)_uR₁₄, COR₁₅, CO₂R₁₆, phenyl or C₃-C₆cycloalkyl groups;

C₁-C₆alkoxy; C₁-C₆haloalkoxy; CN; NO₂; S(O)_uR₁₇; COR₁₈; CO₂R₁₉; phenyl optionally substituted
10 with one or more halogen, CN, C₁-C₃haloalkyl, or C₁-C₃haloalkoxy groups;

C₃-C₆cycloalkyl; or phenylthio;

Q is phenyl optionally substituted with one or more
halogen, CN, SCN, NO₂, S(O)_uR₂₀, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxyalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, or NR₂₁R₂₂ groups;

u is an integer of 0, 1 or 2;

R₁₄, R₁₅, R₁₆, R₁₈, R₁₉, R₂₁ and R₂₂ are each
independently H or C₁-C₆alkyl;

20 R₁₇ and R₂₀ are each independently C₁-C₆alkyl or C₁-C₆haloalkyl;

R₃₃ is CO₂R₃₄;

R₃₄ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, phenyl or
halophenyl; and the dotted line configuration

25 C=N represents a double bond or a single bond (i.e. C-N or C=N); or

a stereoisomer thereof.

Preferred neuronal sodium channel antagonists suitable
for use in the composition of the invention are those
30 compounds of formula I, II or III wherein the dotted line configuration C=N represents a double bond.

More preferred neuronal sodium channel antagonists
suitable for use in the inventive composition are those
compounds of formula I or formula III wherein the dotted
35 line configuration represents a double bond.

10

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X' and Y' are each independently H; halogen; CN; SCN;

C₁-C₆alkyl optionally substituted with one or

more halogen, NO₂, CN, C₁-C₄alkoxy, C₁-

C₄alkylthio, phenyl, halophenyl, C₁-

25

C₁-C₄alkoxycarbonyl groups;

C₂-C₄alkenyl; C₂-C₄haloalkenyl; C₂-C₄alkynyl; C₂-

C₄haloalkynyl; C₃-C₆cycloalkyl; C₃-

C₆halocycloalkyl; phenyl optionally substituted

30

C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy,

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C₁-C₄alkylthio, C₁-C₄alkylsulfonyl or C₁-
C₄haloalkylsulfonyl groups;
C₁-C₄alkylcarbonyl; C₁-C₄haloalkylcarbonyl; or
NR₂₈R₂₉;

5 m is an integer of 1, 2, 3, 4 or 5;

G' is phenyl optionally substituted with one or more
groups which may be the same or different
selected from X';

10 a 5-membered heteroaromatic ring containing one
or two heteroatoms selected from 0 or 1
oxygen, 0 or 1 sulfur and 0, 1 or 2
nitrogen atoms said 5-membered
heteroaromatic ring being attached via
carbon and being optionally substituted
15 with one or more groups which may be the
same or different selected from X'; or

a 6-membered heteroaromatic ring containing one
or two heteroatoms selected from 0 or 1
oxygen, 0 or 1 sulfur and 0, 1 or 2
20 nitrogen atoms said 6-membered
heteroaromatic ring being attached via
carbon and being optionally substituted
with one or more groups which may be the
same or different selected from X';

25 Q' is H; C₁-C₆alkyl optionally substituted with one
or more halogen, CN, C₁-C₃alkoxy, C₁-
C₆alkoxycarbonyl, or phenyl optionally
substituted with one or more halogen,
CN, NO₂, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-
30 C₄alkylsulfonyl or C₁-C₄alkylsulfinyl
groups;

C₂-C₆alkenyl; C₂-C₆alkynyl; or phenyl optionally
substituted with one to three groups,
which may be the same or different,
35 selected from X';

R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} and R_2 , are each independently H or C_1 - C_4 alkyl; and the dotted line configuration $C \equiv N$ represents a double bond or a single bond (i.e. $C-N$ or $C=N$); or
5 a stereoisomer thereof.

Further preferred neuronal sodium channel antagonist compounds of the invention are those compounds of formula IV or V wherein the dotted line configuration $C \equiv N$ represents a double bond.

10 Other preferred neuronal sodium channel antagonist compounds suitable for use in the composition of the invention are those compounds of formula IV or V wherein W is O; X" and Y" are each independently H or C_1 - C_6 haloalkyl; m is 1; R_{23} , R_{24} , R_{25} , R_{26} and R_2 , are each H; G
15 is phenyl optionally substituted with one or more halogen atoms; Q' is halophenyl or C_1 - C_4 alkyl optionally substituted with one phenyl or halophenyl group; and the dotted line configuration $C \equiv N$ represents a double bond; or a stereoisomer thereof.

20 The second active ingredient of the insecticidal composition of the invention includes one or more compounds selected from Group A:

- 1) pyrethroid compounds which are known to be insecticidally active such as cypermethrin, cyhalothrin,
25 cyfluthrin, permethrin or the like;
- 2) pyrethroid-type compounds which are known to be insecticidally active such as ethofenprox, silafluofen, or the like;
- 3) organophosphate compounds which are known to be
30 insecticidally active such as profenofos, acephate, sulprofos, malathion, diazinon, methyl parathion, terbufos, or the like;
- 4) carbamate compounds which are known to be insecticidally active such as methomyl, thiodicarb,
35 fenothiocarb, or the like;

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5) formamidine compounds which are known to be insecticidally active such as amitraz, chlordimeform, hydramethylnon, chlorfenamidine, or the like;

6) macrocyclic lactone compounds which are known to be insecticidally active such as spinosad, avermectin, emamectin, milbemectin, nemadectin, moxidectin or the like;

7) amidinohydrazone compounds which are known to be insecticidally active such as hydramethylnon;

8) GABA antagonist compounds which are known to be insecticidally effective such as fipronil, endosulfan, or the like;

9) acetylcholine receptor ligand compounds which are known to be insecticidally effective such as imidacloprid, acetamiprid, nitenpyram, thiamethoxam, or the like.

Descriptions of the above-listed commercially available compounds may be found in The Pesticide Manual, 11th Edition, British Crop Protection Council (1997) among other publications.

Preferred compositions of the invention are those compositions having a neuronal sodium channel antagonist compound of formula I or formula III in combination with one or more compounds selected from Group A.

More preferred compositions of the invention are those compositions having a formula I or formula III compound wherein W is O; X is trifluoromethoxy and is in the 4-position; Y is trifluoromethyl and is in the 3-position; Z is CN and is in the 4-position; A is CH₃; n is 0; m, p and q are each independently 1; R and R₁ are each independently H; Z' is Cl; R₃ and G are each independently CO₂CH₃; Q is p-(trifluoromethoxy)phenyl; and the dotted line configuration C=N represents a double bond in combination with one or more compounds selected from Group A.

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Each of the compounds of formula I, II, III, IV and V embody assymetric centers which may be represented in the stereoisomeric R-form or S-form. The present invention also includes the R-form, the S-form or
5 mixtures comprising the R-form and the S-form in an arbitrary ratio. For compounds of formula III, the S-form is preferred.

Advantageously, the neuronal sodium-channel antagonist compound of formula I, II, III, IV or V or a mixture
10 thereof may be formulated with a second insecticidally effective ingredient and optionally other customary formulation adjuvants. Said formulation may be dispersed in a solid or liquid diluent for application to the insect, its food supply, breeding ground or habitat as a dilute
15 spray or as a solid dust or dust concentrate.

The active ingredients of the inventive composition may also be formulated separately as a wettable powder, emulsifiable concentrate, aqueous or liquid flowable, suspension concentrate or any one of the conventional
20 formulations used for insect control agents and tank-mixed in the field with water or other inexpensive liquid for application as a liquid spray mixture. The separately formulated compositions may also be applied sequentially.

Advantageously, the composition of the invention may be formulated as a bait composition comprising a synergistically effective amount of a combination of a neuronal sodium channel antagonist plus one or more compounds selected from Group A and a solid or liquid
30 edible nutritive substance. A preferred bait composition may contain by weight about 0.01% to 20% active ingredients, preferably a neuronal sodium channel antagonist in combination with hydramethylnon.

In actual practice, the composition of the invention
35 is applied to the plant foliage or plant stem or insect

habitat as a dilute spray prepared from any of the above-said formulations. The ratio of the essential active ingredients of the composition of the invention is about 1 weight part of a neuronal sodium channel antagonist to
5 about 0.01-100 weight parts of one or more compounds selected from Group A.

The compositions of the invention are superior insecticidal compositions and are especially useful for protecting growing and harvested plants including:
10 leguminous crops such as soybeans, snap beans, peas, wax beans and the like as well as cotton, forage crops, cole crops, leafy vegetables, tobacco, hops, tomatoes, potatoes, flowering ornamentals such as chrysanthemums, vine crops such as grapes, squash, pumpkin or melon and
15 fruit trees such as cherry, peach, apple or citrus, from the ravages of insects.

The synergistic insecticidal composition of the invention is found to be highly active against a wide variety of lepidopteran and coleopteran insects such as
20 *Helicoverpa zea* (cotton bollworm), *Heliothis virescens* (tobacco budworm), *Leptinotarsa decemlineata* (Colorado potato beetle), *Diabrotica spp.* (corn rootworm) and the like.

Also the composition of the invention may be useful for the prevention and control of public health pests
25 such as houseflies, mosquitoes, cockroaches, ants, termites or the like.

Further, the compositions of the invention may be particularly useful for the prevention and control of wood-eating insects such as termites, carpenter ants,
30 wood-destroying beetles or the like.

These and other advantages of the invention may become more apparent from the examples set forth herein below. These examples are provided merely as illustrations of the invention and are not intended to be construed as a
35 limitation thereof.

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EXAMPLE 1

Evaluation of the Synergistic Insecticidal Effect of
a Combination of a Neuronal Sodium Channel Antagonist
5 Plus a Second Insecticide

In this evaluation, *Heliothis zea* (cotton bollworm),
Heliothis virescens (tobacco budworm) and pyrethroid-
resistant *Heliothis virescens* larvae used are obtained
from laboratory colonies. Pyrethroid-resistant *H.*
10 *virescens* are derived from the PEG-strain [Campannola² &
Plapp, Proceedings of Beltwide Cotton Conference (1988)].

Cotton leaves are immersed in 1:1 v/v, acetone/water
solutions of test compound, or solutions of a combination
of test compounds for a period of about 3 seconds.
15 Following immersion, leaves are allowed to air-dry for 2-3
hours. Plastic bioassay trays containing multiple open-
faced wells (4.0 x 4.0 x 2.5 cm) are used as the test
arenas. Cut portions of a treated leaf, a moistened
cotton dental wick and a single third-instar larva are
20 placed into each well, covered with an adhesive vented
clear plastic sheet and held under constant fluorescent
light at about 27°C for a predetermined period of time.
Larval mortality/morbidity is evaluated at 5 days after
treatment. All treatments are replicated 4-5 fold in a
25 randomized complete block design with 16-32 larvae per
treatment. Using conventional log-probit analysis, the
LC₅₀ of each treatment is determined.

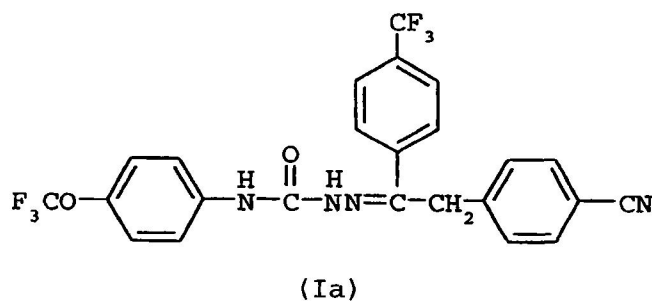
Using the above protocol, a neuronal sodium channel
antagonist (Compound A) is evaluated alone at dose rates
30 of 0.1 ppm, 1.0 ppm and 10.0 ppm and in combination with
1.0 ppm of a second insecticidal compound. The treatments
used are shown in Table I.

Each of the combinations evaluated demonstrates
synergistic insecticidal activity.

Table I

Second Active Compound	Dose Rate (ppm)	Compound A ¹			
		Dose Rate			
		(ppm)	(ppm)	(ppm)	(ppm)
cypermethrin	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
amitraz	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
fipronil	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
acetamiprid	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
spinosad	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
thiodicarb	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0

¹Compound A = formula Ia neuronal sodium channel antagonist



EXAMPLE 2Evaluation of the Synergistic Insecticidal Effect Of
a Combination Of A Neuronal Sodium Channel Antagonist
Plus an Amidinohydrazone

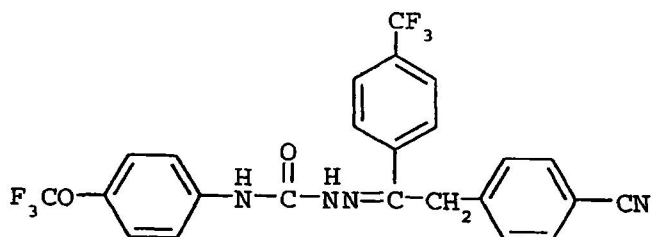
In this evaluation, adult male German cockroaches (*Blattella germanica*) are used. For each test, a 4.0 g portion of ground Purina Dog Chow (Hi-Pro Glo®) is treated with an acetone solution of test compound alone or in combination with a second test compound. After treatment, the acetone is evaporated and the treated dog chow is placed in a 3/4 oz plastic cup which is placed in a harborage made of folded sheets of blotter paper placed in a plastic box (16"L x 11"W x 6"H). The plastic box (test arena) is also fitted with a 1 oz narrow mouth bottle with 2 dental wicks inserted at the mouth. A control box is prepared in the same manner using ground dog chow which has been treated with reagent grade acetone. Each treatment is replicated three times. Into each test arena are placed 20 healthy adult male cockroaches which have been reared in an insectary. The test arenas are then stored at 76°F and mortality is determined daily by visual examination. The data obtained are shown in Table II.

Table II

Test Compound	% Active Ingredient	% Mortality					
		Days After Treatment					
		3	4	5	6	7	8
A ¹	0.05	0	0	0	0	0	0
A	0.10	1.7	11.7	11.7	11.7	18.3	18.3
A	0.50	5.0	5.0	5.0	5.0	5.0	5.0
B ²	1.00	0	5.0	28.3	71.7	90.0	93.3
A+B	0.05+1.0	0	20.0	41.7	81.7	95.0	98.3
A+B	0.10+1.0	0	21.7	51.7	88.3	95.0	95.0
A+B	0.50+1.0	16.7	58.3	80.0	95.0	98.3	100.0
Control	0	0	1.7	3.3	3.3	3.3	5.0

¹Compound A = formula Ia neuronal sodium channel antagonist

²Compound B = hydramethylnon



(Ia)

As can be seen from the data shown in Table II, combinations of a neuronal sodium channel antagonist plus an amidinohydrazone insecticide demonstrate synergistic insect control.

WHAT IS CLAIMED IS:

- 1 2. The composition according to claim 1 having a
2 neuronal sodium channel antagonist compound of formula



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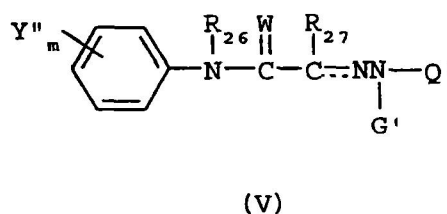
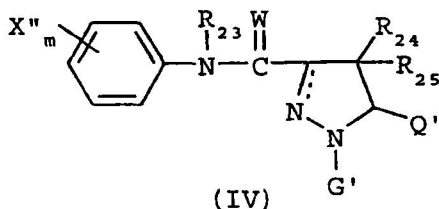
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1 substituted with one or more halogen, C₁-
 2 C₃alkoxy, C₁-C₃haloalkoxy, C₃-C₆cycloalkyl,
 3 C₂-C₆alkenyloxy or sulfonyloxy groups;
 4 C₁-C₆alkoxy optionally substituted with one or
 5 more halogen, C₁-C₃alkoxy or C₃-C₆cycloalkyl
 6 groups;
 7 C₁-C₆alkoxycarbonyl, C₃-C₆cycloalkylcarbonyloxy,
 8 phenyl optionally substituted with one or
 9 more halogen, C₁-C₄alkyl, or C₁-C₄alkoxy
 10 groups;
 11 aminocarbonyloxy optionally substituted with
 12 one or more C₁-C₃alkyl groups;
 13 C₁-C₆alkoxycarbonyloxy; C₁-C₆alkylsulfonyloxy;
 14 C₂-C₆alkenyl; or NR₁₂R₁₃;
 15 m, p and q are each independently an integer of 1,
 16 2, 3, 4, or 5;
 17 n is an integer of 0, 1 or 2;
 18 r is an integer of 1 or 2;
 19 t is an integer of 1, 2, 3 or 4;
 20 R, R₁, R₂, R₃, R₄ and R₅ are each independently H or
 21 C₁-C₄alkyl;
 22 R₆ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxyalkyl,
 23 C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyl, C₂-
 24 C₆alkynyl, C₁-C₆alkylcarbonyl, C₁-C₆alkoxy-
 25 carbonyl, C₁-C₆alkylthio, or C₁-C₆haloalkylthio;
 26 R₇ and R₈ are each independently H; halogen; C₁-
 27 C₆alkyl; C₁-C₆alkylcarbonyloxy; or phenyl
 28 optionally substituted with one or more
 29 halogen, CN, NO₂, C₁-C₆alkyl, C₂-C₆halo-
 30 alkyl, C₁-C₆alkoxy or C₁-C₆haloalkoxy
 31 groups;
 32 R₉ and R₁₀ are each independently H, or C₁-C₄alkyl;
 33 R₁₁ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-
 34 C₄alkylcarbonyl, C₁-C₆alkoxycarbonyl, or C₁-
 35 C₆haloalkoxycarbonyl;

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36 R_{12} and R_{13} are each independently H or C_1-C_6 alkyl;
 37 G is H; C_1-C_6 alkyl optionally substituted with one or
 38 more halogen, C_1-C_4 alkoxy, C_1-C_6 haloalkoxy,
 39 CN, $NO_2S(O)_uR_{14}$, COR_{15} , CO_2R_{16} , phenyl or C_3-
 40 C_6 cycloalkyl groups;
 41 C_1-C_6 alkoxy; C_1-C_6 haloalkoxy; CN; NO_2 ; $S(O)_uR_{17}$;
 42 COR_{18} ; CO_2R_{19} ; phenyl optionally substituted
 43 with one or more halogen, CN, C_1-C_3 halo-
 44 alkyl, or C_1-C_3 haloalkoxy groups;
 45 C_3-C_6 cycloalkyl; or phenylthio;
 46 Q is phenyl optionally substituted with one or more
 47 halogen, CN, SCN, NO_2 , $S(O)_uR_{20}$, C_1-C_4 alkyl, C_1-
 48 C_4 haloalkyl, C_1-C_4 alkoxyalkyl, C_1-C_6 alkoxy, C_1-
 49 C_6 haloalkoxy, or $NR_{21}R_{22}$ groups;
 50 u is an integer of 0, 1 or 2;
 51 R_{14} , R_{15} , R_{16} , R_{18} , R_{19} , R_{21} and R_{22} are each
 52 independently H or C_1-C_6 alkyl;
 53 R_{17} and R_{20} are each independently C_1-C_6 alkyl or
 54 C_1-C_6 haloalkyl;
 55 R_{33} is CO_2R_{34} ;
 56 R_{34} is H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, phenyl or
 57 halophenyl; and the dotted line configuration
 58 $C \equiv N$ represents a double bond or a single bond; or
 59 a stereoisomer thereof.

1 3. The composition according to claim 1
 2 having a neuronal sodium channel antagonist compound of
 3 formula
 4
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7 wherein W is O or S;
 8 X" and Y" are each independently H; halogen; CN; SCN;
 9 C₁-C₆alkyl optionally substituted with one or
 10 more halogen, NO₂, CN, C₁-C₄alkoxy, C₁-
 11 C₄alkylthio, phenyl, halophenyl, C₁-
 12 C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl, or
 13 C₁-C₄alkoxycarbonyl groups;
 14 C₂-C₄alkenyl; C₂-C₄haloalkenyl; C₂-C₄alkynyl; C₂-
 15 C₄haloalkynyl; C₃-C₆cycloalkyl; C₃-
 16 C₆halocycloalkyl; phenyl optionally substituted
 17 with one or more halogen, CN, NO₂, C₁-C₄alkyl,
 18 C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy,
 19 C₁-C₄alkylthio, C₁-C₄alkylsulfonyl or C₁-
 20 C₄haloalkylsulfonyl groups;
 21 C₁-C₄alkylcarbonyl; C₁-C₄haloalkylcarbonyl; or
 22 NR₂,R₂;
 23 m is an integer of 1, 2, 3, 4 or 5;
 24 G' is phenyl optionally substituted with one or more
 25 groups which may be the same or different
 26 selected from X";
 27 a 5-membered heteroaromatic ring containing one
 28 or two heteroatoms selected from 0 or 1
 29 oxygen, 0 or 1 sulfur and 0, 1 or 2
 30 nitrogen atoms said 5-membered
 31 heteroaromatic ring being attached via
 32 carbon and being optionally substituted
 33 with one or more groups which may be the
 34 same or different selected from X"; or
 35 a 6-membered heteroaromatic ring containing one
 36 or two heteroatoms selected from 0 or 1
 37 oxygen, 0 or 1 sulfur and 0, 1 or 2
 38 nitrogen atoms said 6-membered
 39 heteroaromatic ring being attached via
 40 carbon and being optionally substituted

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41 with one or more groups which may be the
42 same or different selected from X';
43 Q' is H; C₁-C₆alkyl optionally substituted with one
44 or more halogen, CN, C₁-C₃alkoxy, C₁-
45 C₆alkoxycarbonyl, or phenyl optionally
46 substituted with one or more halogen,
47 CN, NO₂, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-
48 C₄alkylsulfonyl or C₁-C₄alkylsulfinyl
49 groups;
50 C₂-C₆alkenyl; C₂-C₆alkynyl; or phenyl optionally
51 substituted with one to three groups,
52 which may be the same or different,
53 selected from X';
54 R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈ and R₂₉ are each
55 independently H or C₁-C₄alkyl; and the dotted
56 line configuration C=N represents a double bond or
57 a single bond; or
58 a stereoisomer thereof.

1 4. The composition according to claim 2 wherein
2 the neuronal sodium channel antagonist is a compound of
3 formula I or III.

1 5. The composition according to claim 4 wherein
2 the dotted line configuration C=N represents a double
3 bond.

1 6. The composition according to claim 5 wherein
2 the compound of formula III is in the S-form.

1 7. The composition according to claim 6 wherein W
2 is O; X is trifluoromethoxy and is in the 4-position; Y
3 is trifluoromethyl and is in the 3-position; Z is CN and
4 is in the 4-position; A is CH₂; n is 0; m, p and q are

5 each 1; R and R₁ are each H; Z' is Cl; R₂, and G are each
6 CO₂CH₃; and Q is p-(trifluoromethoxy)phenyl.

1 8. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 cypermethrin, cyhalomethrin, cyfluthrin, permethrin,
4 ethofenprox or silafluofen.

1 9. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 profenofos, acephate, sulprofos, malathion, diazinon,
4 methyl parathion, or terbufos.

1 10. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 methonyl, thiodicarb, or fenothiocarb.

1 11. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 amitraz, chlordimeform, or chlorfenamidin.

1 12. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 avermectin, emamectin, milbemectin, nemadectin, or
4 moxidectin.

1 13. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A is
3 hydramethylnon.

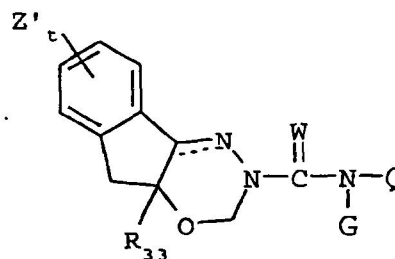
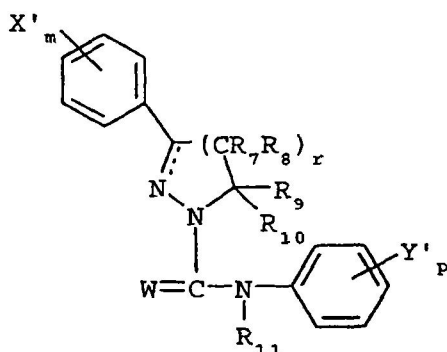
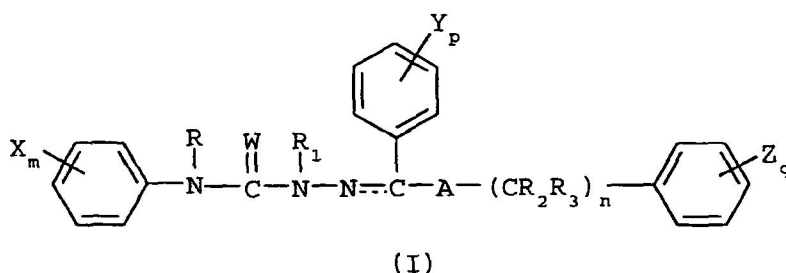
1 14. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 fipronil, endosulfon, imidacloprid, acetamiprid,
4 nitenpyram or thiamethoxam.

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1 15. A method for synergistic insect control which
2 comprises contacting said insect with a synergistically
3 effective amount of a neuronal sodium channel antagonist
4 in combination with one or more compounds selected from
5 Group A.

1 16. The method according to claim 15 having a
2 neuronal sodium channel antagonist compound of formula
3



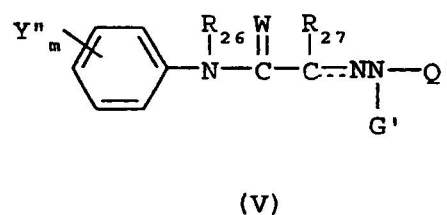
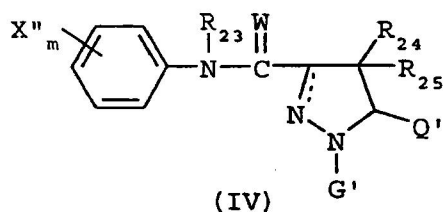
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9 wherein A is CR₄R₅ or NR₆;
10 W is O or S;
11 X, Y, Z, X', Y' and Z' are each independently H;
12 halogen; OH; CN; NO₂; C₁-C₆alkyl optionally
13 substituted with one or more halogen, C₁-
14 C₃alkoxy, C₁-C₃haloalkoxy, C₃-C₆cycloalkyl,
15 C₂-C₆alkenyloxy or sulfonyloxy groups;
16 C₁-C₆alkoxy optionally substituted with one or

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17 more halogen, C₁-C₃alkoxy or C₃-C₆cycloalkyl
18 groups;
19 C₁-C₆alkoxycarbonyl, C₃-C₆cycloalkylcarbonyloxy,
20 phenyl optionally substituted with one or
21 more halogen, C₁-C₄alkyl, or C₁-C₄alkoxy
22 groups;
23 aminocarbonyloxy optionally substituted with
24 one or more C₁-C₃alkyl groups;
25 C₁-C₆alkoxycarbonyloxy; C₁-C₆alkylsulfonyloxy;
26 C₂-C₆alkenyl; or NR₁₂R₁₃;
27 m, p and q are each independently an integer of 1,
28 2, 3, 4, or 5;
29 n is an integer of 0, 1 or 2;
30 r is an integer of 1 or 2;
31 t is an integer of 1, 2, 3 or 4;
32 R, R₁, R₂, R₃, R₄ and R₅ are each independently H or
33 C₁-C₄alkyl;
34 R₆ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxyalkyl,
35 C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyl, C₂-
36 C₆alkynyl, C₁-C₆alkylcarbonyl, C₁-C₆alkoxy-
37 carbonyl, C₁-C₆alkylthio, or C₁-C₆haloalkylthio;
38 R₇ and R₈ are each independently H; halogen; C₁-
39 C₆alkyl; C₁-C₆alkylcarbonyloxy; or phenyl
40 optionally substituted with one or more
41 halogen, CN, NO₂, C₁-C₆alkyl, C₂-C₆halo-
42 alkyl, C₁-C₆alkoxy or C₁-C₆haloalkoxy
43 groups;
44 R₉ and R₁₀ are each independently H, or C₁-C₄alkyl;
45 R₁₁ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-
46 C₄alkylcarbonyl, C₁-C₆alkoxycarbonyl, or C₁-
47 C₆haloalkoxycarbonyl;
48 R₁₂ and R₁₃ are each independently H or C₁-C₆alkyl;
49 G is H; C₁-C₆alkyl optionally substituted with one or
50 more halogen, C₁-C₄alkoxy, C₁-C₆haloalkoxy,
51 CN, NO₂S(O)_vR₁₄, COR₁₅, CO₂R₁₆, phenyl or C₃-

52 C₆cycloalkyl groups;
 53 C₁-C₆alkoxy; C₁-C₆haloalkoxy; CN; NO₂; S(O)_uR₁₇;
 54 COR₁₈; CO₂R₁₉; phenyl optionally substituted
 55 with one or more halogen, CN, C₁-C₃halo-
 56 alkyl, or C₁-C₃haloalkoxy groups;
 57 C₃-C₆cycloalkyl; or phenylthio;
 58 Q is phenyl optionally substituted with one or more
 59 halogen, CN, SCN, NO₂, S(O)_uR₂₀, C₁-C₄alkyl, C₁-
 60 C₄haloalkyl, C₁-C₄alkoxyalkyl, C₁-C₆alkoxy, C₁-
 61 C₆haloalkoxy, or NR₂₁R₂₂ groups;
 62 u is an integer of 0, 1 or 2;
 63 R₁₄, R₁₅, R₁₆, R₁₈, R₁₉, R₂₁ and R₂₂ are each
 64 independently H or C₁-C₆alkyl;
 65 R₁₇ and R₂₀ are each independently C₁-C₆alkyl or
 66 C₁-C₆haloalkyl;
 67 R₃₃ is CO₂R₃₄;
 68 R₃₄ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, phenyl or
 69 halophenyl; and the dotted line configuration
 70 C=N represents a double bond or a single bond; or
 71 a stereoisomer thereof.

1 17. The method according to claim 15 having a
 2 neuronal sodium channel antagonist compound of formula
 3
 4



5 wherein W is O or S;
 6
 7 X' and Y' are each independently H; halogen; CN; SCN;
 8 C₁-C₆alkyl optionally substituted with one or
 9 more halogen, NO₂, CN, C₁-C₄alkoxy, C₁-
 10

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11 C₄alkylthio, phenyl, halophenyl, C₁-
 12 C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl, or
 13 C₁-C₄alkoxycarbonyl groups;
 14 C₂-C₄alkenyl; C₂-C₄haloalkenyl; C₂-C₄alkynyl; C₂-
 15 C₄haloalkynyl; C₃-C₆cycloalkyl; C₃-
 16 C₆halocycloalkyl; phenyl optionally substituted
 17 with one or more halogen, CN, NO₂, C₁-C₄alkyl,
 18 C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy,
 19 C₁-C₄alkylthio, C₁-C₄alkylsulfonyl or C₁-
 20 C₄haloalkylsulfonyl groups;
 21 C₁-C₄alkylcarbonyl; C₁-C₄haloalkylcarbonyl; or
 22 NR₂R₂;
 23 m is an integer of 1, 2, 3, 4 or 5;
 24 G' is phenyl optionally substituted with one or more
 25 groups which may be the same or different
 26 selected from X';
 27 a 5-membered heteroaromatic ring containing one
 28 or two heteroatoms selected from 0 or 1
 29 oxygen, 0 or 1 sulfur and 0, 1 or 2
 30 nitrogen atoms said 5-membered
 31 heteroaromatic ring being attached via
 32 carbon and being optionally substituted
 33 with one or more groups which may be the
 34 same or different selected from X'; or
 35 a 6-membered heteroaromatic ring containing one
 36 or two heteroatoms selected from 0 or 1
 37 oxygen, 0 or 1 sulfur and 0, 1 or 2
 38 nitrogen atoms said 6-membered
 39 heteroaromatic ring being attached via
 40 carbon and being optionally substituted
 41 with one or more groups which may be the
 42 same or different selected from X';
 43 Q' is H; C₁-C₆alkyl optionally substituted with one
 44 or more halogen, CN, C₁-C₃alkoxy, C₁-
 45 C₆alkoxycarbonyl, or phenyl optionally

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46 substituted with one or more halogen,
47 CN, NO₂, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-
48 C₄alkylsulfonyl or C₁-C₄alkylsulfinyl
49 groups;
50 C₂-C₆alkenyl; C₂-C₆alkynyl; or phenyl optionally
51 substituted with one to three groups,
52 which may be the same or different,
53 selected from X';
54 R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈ and R₂₉ are each
55 independently H or C₁-C₄alkyl; and the dotted
56 line configuration C=N represents a double bond or
57 a single bond; or
58 a stereoisomer thereof.

1 18. The method according to claim 16 wherein the
2 neuronal sodium channel antagonist is a compound of
3 formula I or III.

1 19. The method according to claim 18 wherein the
2 dotted line configuration C=N represents a double bond.

1 20. The method according to claim 19 wherein the
2 formula III compound is in the S-form.

3 21. The method according to claim 20 wherein W is
4 O; X is trifluoromethoxy and is in the 4-position; Y is
5 trifluoromethyl and is in the 3-position; Z is CN and is
6 in the 4-position; A is CH₂; n is 0; m, p and q are each
7 1; R and R1 are each H; Z' is Cl; R₃₃ and G are each
8 CO₂CH₃; and Q is p-(trifluoromethoxy)phenyl.

1 22. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 cypermethrin, cyhalomethrin, cyfluthrin, permethrin,
4 ethofenprox or silafluofen.

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1 23. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 profenofos, acephate, sulprofos, malathion, diazinon,
4 methyl parathion, or terbufos.

1 24. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 methonyl, thiodicarb, or fenothiocarb.

1 25. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are amitraz,
3 chlordimeform, or chlorfenamidine.

1 26. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 avermectin, emamectin, milbemectin, nemadectin, or
4 moxidectin.

1 27. The method according to claim 21 wherein the
2 one or more compounds selected from Group A is
3 hydramethylnon.
4

1 28. The method according to claim 21 wherein the one
2 or more compounds selected from Group A are fipronil,
3 endosulfon, imidacloprid, acetamiprid, nitenpyram or
4 thiamethoxam.

1 29. A method for protecting a plant from infestation
2 and attack by insects which comprises applying to the
3 foliage or stem of said plant a synergistically effective
4 amount of a composition according to claim 1.

1 30. The method according to claim 29 wherein the
2 insects are *lepidoptera* or *coleoptera*.

Abril 6, 2000
Traducción Oficial No.0244
REF: AMERICAN HOME PRODUCTS CORP
Patente No.60/158,201

(American Cyanamid Company)
Caso-33,562-00

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DEPARTAMENTO DE COMERCIO DE LOS ESTADOS
UNIDOS
OFICINA DE MARCAS Y PATENTES

Marzo 28, 2000

Por medio del presente documento se certifica que adjunta se encuentra una fiel copia de los registros de la Oficina de Marcas y Patentes de los Estados Unidos, correspondientes a los documentos para la solicitud tal como se presentaron, con el fin de asignarle una fecha de registro bajo la norma del código 35 USC 111.

Número de Solicitud: 60/158,201

Fecha de Registro: Octubre, 1999

Autorizado por:

COMISIONADO DE MARCAS Y PATENTES

Firma: P. SWAIN

Funcionario Encargado de Certificaciones

Hay sello de la Oficina de Marcas y Patentes de color dorado.

Edna de Caluso

Assistant Commissioner for Patents
Box Patent Application
Washington, D.C. 20231

Caso No:33562-01L

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SOLICITUD PROVISIONAL

Por medio de la presente se realizan los trámites necesarios para la solicitud de patente de los siguientes inventor(es).

Michael Frank Treacy, Paul E. Resner, Raymond Frank Borysewicz;
Hassan Oloumi, Kurt Allen Schwinghammer;
para el invento: COMPOSICIONES SINERGETICAS PARA
INSECTICIDAS

1. Se adjuntan Documentos requeridos para el registro bajo el código 37 CFR 1.51(a) (2) y 1.53(b) (2):
 - 16 páginas para especificación
 - 12 páginas de Reivindicaciones
 - 1 Página (s) de Resumen
 - Páginas de Gráficas
 - ☐ Formal
 - ☐ Informal
2. Nombres de inventor(es) y dirección (es) (o lista de abogados en el caso como identificador alfanumérico):

Michael Frank Treacy

Edvardo Calado

53 Sequoia Drive
Newtown, PA 18940

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Paul Resner
1267 Woodthrush Court
Yardley, PA 19067

Raymond Frank Borysewicz
12 Albermarle Road
Hamilton Square, NJ 08690

Kurt Allen Schwinghammer
1206 University Drive
Yardley, PA 19067

Hassan Oloumi
1204 Goldenrod Court
Yardley, PA

3. Traspaso

Se realiza un traspaso del invento a:

American Cyanamid Company
5 Giralda Farms
Madison, New Jersey 07940-0874

Eduardo Calado

☐ Fue realizada en la solicitud anterior y registrada como PTO
en _____, Carrete _____, Cuadro.

☐ Se adjunta bajo Formulario de Registro por separado.

☒ a continuación.

CERTIFICADO DE ENVIO POSTAL BAJO CÓDIGO 37 CFR 1.10

Yo, por medio del presente documento certifico que este ha sido enviado por Servicio Postal del Correo de los Estados Unidos de América, en la fecha anteriormente mencionada en un sobre rotulado "Correo Postal al Destinatario" con número de envío: TB13073433X US, rotulado al Comisionado Asistente para Patentes, Box Patent Application, Washington, DC., 20231.

Firma: Barbara Lences

Fecha: Octubre 7, 1999

4. Registro de Honorarios \$150.00

5. Método de pago de Honorarios:

Eduardo Calado R. 4

Cobrar a la cuenta corriente No 01-1300 por la suma de \$150.00
Se adjunta un duplicado del trámite.

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6. Instrucciones en caso de que se registre un Sobre pago:
Acreditar cualquier sobre pago a la cuenta bancaria No. 01-1300.

7. Autorización para Cobros Adicionales de Honorarios

[x] El comisionado se encuentra autorizado para cobrar cualquier honorario adicional que se presente en este documento y durante la vigencia de esta solicitud a la Cuenta Corriente No. 01-1300:

[x] 37 CFR 1.51(a), (2) y 1.53 (c) registro de honorarios

[x] recargo para registro de honorarios básicos y/o primera página en una fecha posterior de la fecha registrada de esta solicitud.

8. Abogados/Nombres de representantes/No. de Registro

John W. Hogan, Jr.	Reg No. 32,703
William H. Calnan	Reg No. 29,520
Charles F. Costello	Reg No. 27, 324
Gregory M. Hill	Reg No. 31,369
Joseph M. Mazzaresse	Reg No. 32,803
Barbara L. Renda	Reg No. 27, 626

Eduardo Calado

Barbara L. Lences

Reg No. 41,148

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9. Dirección para correspondencia

John W. Hogan, Jr.

American Home Products Corporation

Patent Law Department

One Campus Drive

Parsippany, NJ 07054

Tel: (973) 683-2152

10. El invento fue realizado por una agencia del Gobierno de los Estados Unidos o bajo Contrato con una agencia del Gobierno de los Estados Unidos.

☒ No

☐ Si, el nombre de dicha Agencia del Gobierno de los Estados Unidos y número de contrato son los siguientes:

Firma: Barbara L. Lences.

No de Registro: 41,148

American Home Products Corporation

Patent Law Department

One Campus Drive

Eduardo Calado

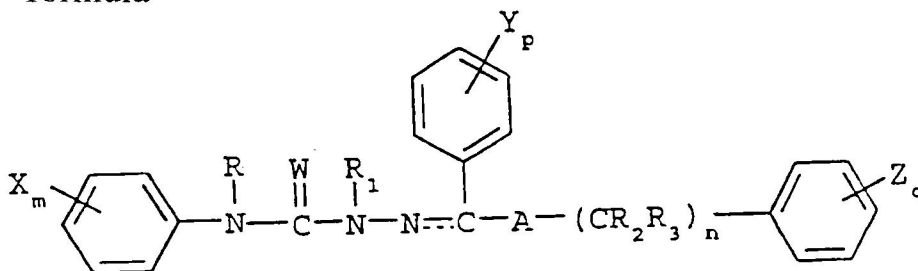
Parsippany, NJ 07054

Tels. No. (973) 683-2152

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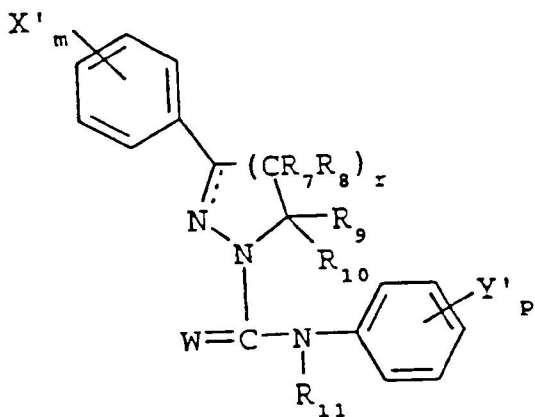
REIVINDICACIONES :

1. Una composición sinérgica insecticida la cual consta de una cantidad sinérgicamente eficaz de un canal de neuronal de sodio antagonista mezclado con uno o más compuestos seleccionados del grupo A.
2. La composición de acuerdo a la reivindicación 1 la cual tiene un compuesto de un canal neuronal de sodio antagonista de la formula

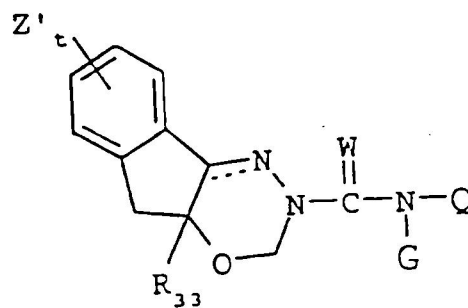


(I)

Edward Calado



(II)



(III)

en el cual A es CR₄R₅ o NR₆;

W es O o S;

X, Y, Z, X', Y', y Z' son cada uno independientemente H;

halógeno; OH; CN; NO₂; C₁-C₆- alquilo opcionalmente

sustituido con uno o más halógenos, C₁-C₃ alcoxi, C₁-C₃

haloalcoxi, C₃-C₆ cicloalquilo, C₂-C₆ alquenilo o grupos

de sulfonilo;

C₁-C₆ alcoxi opcionalmente sustituidos con uno o más halógenos,

C₁-C₃-alcoxi o C₃-C₆ grupos de cicloalquilo;

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C1-C6 alcoxycarbonilo, C3-C6 cicloalquilocarboniloxi, fenilo
opcionalmente sustituido con uno o más halógenos, C1-C4 alquilo o
C1-C4 grupos de alcoxi;

aminocarboniloxi opcionalmente sustituido por uno o más grupos de
C1-C3- alquilo;

C1-C6 alcoxycarboniloxi; C1-C6 alquilosulfoniloxi;
C2-C6 alquenilo; o NR12R13;

m, p y q son cada uno un número entero de 1, 2, 3, 4, o 5;

n es un número entero de 0, 1 o 2;

r es un número entero de 1 hasta 2;

t es un número entero de 1, 2, 3, o 4;

R, R1, R2, R3, R4 y R5 son cada uno independientes de H o C1-C4
alquilo;

R6 es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C6 alcoxialquilo, C1-
C6 alcoxi, C1-C6 haloalcoxi, C2-C6 alquenilo, C2-C6 alquenilo, C2-
C6 alquinilo, C1-C6 alquilocarbonilo, C1-C6 alcoxycarbonilo, C1-C6
alquiltio, o C1-C6 haloalquiltio;

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R7 y R8 son cada uno independientes de H; halógeno; C1-C6alquilo;
C1-C6 alquilocarbonilo; o fenilo opcionalmente sustituido con uno
o más halógenos, CN, NO₂, C1-C6alquilo, C2-C6 haloalquilo, C1-
C6alcoxi o C1-C6 grupos de haloalcoxi;

R9 y R10 son cada uno independientes de H, o C1-C4alquilo;
R11 es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C4
alquilocarbonilo, C1-C6 alcoxicarbonilo o C1-C6
haloalcoxicarbonilo;

R12 y R13 son cada uno independientes de H o C1-C6 alquilo;
G es H; C1-C6 alquilo opcionalmente sustituido con uno o más
halógenos, C1-C4 alcoxi, C1-C6haloalcoxi, CN, NO₂S (O)uR14,
COR15, CO₂R16, fenilo o C3-C6 grupos de cicloalquilo;

C1-C6alcoxi; C1-C6 haloalcoxi; CN; NO₂; S(O)u R17; COR18;
CO₂R19; fenilo opcionalmente sustituido con uno o más halógenos,
CN, C1-C3 haloalquilo o C1-C3 grupos de haloalquilo;

C3-C6 cicloalquilo; Feniltio;

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Q es fenilo opcionalmente sustituido con uno o más halógenos, CN, SCN, NO₂, S(O)_uR₂₀, C1-C4 alquilo, C1-C4 haloalquilo, C1-C4 alcoxialquilo, C1-C6 alcoxi, C1-C6 haloalcoxi, o grupos de NR₂₁R₂₂;

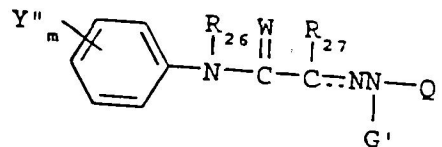
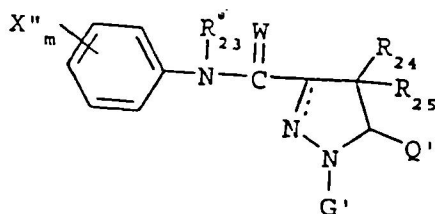
R₁₄, R₁₅, R₁₆, R₁₈, R₁₉, R₂₁ y R₂₂ son cada uno independientes de H o C1-C6 alquilo;

R₁₇ y R₂₀ son cada uno independientes de C1-C6 alquilo o C1-C6 haloalquilo;

R₃₃ es CO₂R₃₄;

R₃₄ es H, C1-C6 alquilo, C1-C6 haloalquilo, fenilo o halofenilo; y la configuración de la línea de puntos C-.N representa un doble enlace o un enlace único; o un estereoisómero del mismo.

3. La composición de acuerdo a la reivindicación 1 la cual tiene un compuesto de un canal neuronal de sodio antagonista de la formula:



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(IV)

(V)

en el cual W es O u S;

X' y Y' son independientes de H; halógeno; CN; SCN; C1-C6 alquilo
opcionalmente sustituido con uno o más halógenos, NO₂, CN, C1-C4
alcoxi, C1-C4 alquiltio, fenilo, halofenilo, C1-C4 alquilosulfonilo,
C1-C4 haloalquilosulfonilo o C1-C4 grupos de alcoxycarbonilo;

C2-C4 alquenilo, C2-C4 haloalquenilo, C2-C4 alquinilo; C2-C4
haloalquinilo; C3-C6 cicloalquilo; C3-C6 halocicloalquilo; fenilo
opcionalmente sustituido con uno o mas halógenos, CN, NO₂, C1-C4
alquilo, C1-C4 haloalquilo, C1-C4alcoxi, C1-C4 haloalcoxi, C1-C4
alquiltio, C1-C4 alquilosulfonilo o grupos de C1-C4
haloalquilosulfonilo;

C1- C4 alquilocarbonilo; C1-C4 haloalquilocarbonilo; o NR₂₈R₂₉;

m es un número entero de 1, 2, 3, 4, o 5;

G' es fenilo opcionalmente sustituido con uno o más grupos los
cuales pueden ser iguales o diferentes seleccionados de X' ;

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un anillo heteroaromatico de 5 miembros que contiene de uno a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1 azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo heteroaromatico de 5 miembros el cual se encuentra unido por medio del carbono y este puede ser opcionalmente sustituido con uno o más grupos, los cuales pueden ser iguales o diferentes, seleccionados de X'; o

un anillo heteroaromatico de 6 miembros que contiene de uno a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1 azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo heteroaromatico de 6 miembros el cual se encuentra unido por medio del carbono y este puede ser opcionalmente sustituido con uno o más grupos, los cuales pueden ser iguales o diferentes, seleccionados de X';

Q es H; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, CN, C1-C3 alcoxi, C1-C6 alcóxicarbonilo o fenilo opcionalmente sustituido con uno o más halógenos, CN, NO₂, C1-C4 alquilo, C1-C4 haloalquilo, C1-C4 alquilosulfonilo o grupos de C1-C4 alquilosulfonilo;

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C2- C6 alquenilo; C2-C6 alquinilo; o fenilo opcionalmente sustituido con uno o hasta tres grupos, los cuales pueden ser iguales o diferentes, seleccionados de X' ;

R23, R24, R25, R26, R27, R28 y R29 son cada uno independientes de H o C1-C4 alquilo; y la configuración de la línea de puntos C.-.N representa un enlace doble o un enlace sencillo; o un estereoisómero del mismo.

4. La composición de acuerdo a la reivindicación 2 en la cual el canal neuronal de sodio antagonista es un compuesto de acuerdo a la formula I o III.

5. La composición de acuerdo a la reivindicación 4 en la cual la configuración de la linea de puntos C.-.N representa un doble enlace.

6. La composición de acuerdo a la reivindicación 5 en la cual el compuesto de la formula III se encuentra en la forma S.

7. La composición de acuerdo a la reivindicación 6 en la cual

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W es O; X es trifluorometoxi y se encuentra en la 4 posición; Y es trifluorometoxi y se encuentra en la 3 -posición; Z es CN y se encuentra en la 4-posición; A es CH₂; n es 0; m, p y q son cada uno independientes de 1; R y R1 son cada uno independientes de H; Z' es Cl; R33 y G son cada uno independientes de CO₂CH₃; y Q es p-(trifluorometoxi) fenilo.

8. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del grupo A son cipermetrina, cihalometrina, ciflutrin, permetrin, etofenprox o silafluofen.

9. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del Grupo A son profenofos, acefato, sulprofos, malation, diazinon, metilo paration o terbufos.

10. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del grupo A son metonilo, tiodicarbo o fenotiocarbo.

11. La composición de acuerdo a la reivindicación 7 en la cual uno o más compuestos seleccionados del grupo A son amitraz, clorodimeform o clorofenamidina.

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12. La composición de acuerdo a la reivindicación 7 en la cual el o los compuestos seleccionados del grupo A son avermectina, anamectina, milbemectina, nemadectina, o moxidectina.

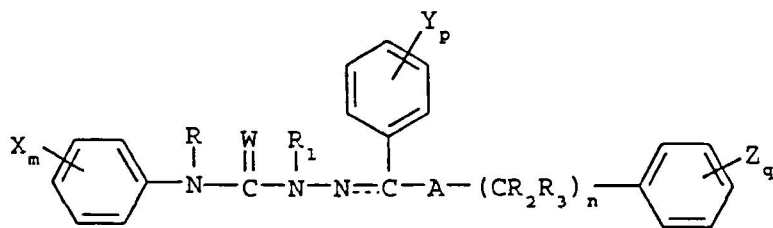
13. La composición de acuerdo a la reivindicación 7 en la cual el o los compuestos seleccionados del grupo A son hidrametilnon.

14. La composición de acuerdo a la reivindicación 7 en la cual el o los compuestos seleccionados del grupo A son fipronil, endosulfon, imidacloprid, acetamiprid, nitenpiram o tiametoxam.

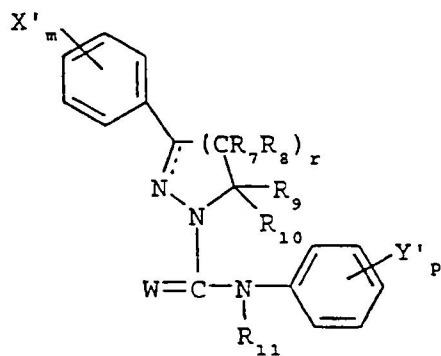
15. Un método para el control sinérgico de insectos el cual consiste en hacer contacto con dicho insecto con una cantidad sinérgicamente eficaz de un canal neuronal de sodio antagonista combinado con uno o más compuestos seleccionados del grupo A.

16. El método de acuerdo a reivindicación 15 el cual tiene un compuesto de un canal neuronal de sodio antagonista de la fórmula:

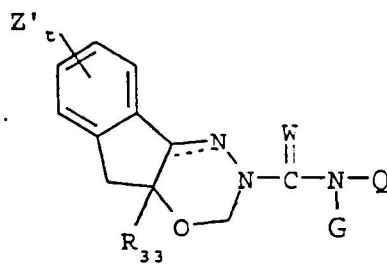
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(I)



(II)



(III)

Charles Calos

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en el cual A es CR₄R₅ o NR₆;

W es O o S;

X, Y, Z, X', Y', y Z' son cada uno independientemente H;

halógeno; OH; CN; NO₂; C₁-C₆- alquilo opcionalmente
sustituido con uno o más halógenos , C₁-C₃ alcoxi, C₁-C₃
haloalcoxi, C₃-C₆ cicloalquilo, C₂-C₆ alquenilo o grupos
de sulfonilo;

C₁-C₆ alcoxi opcionalmente sustituidos con uno o más halógenos,
C₁-C₃-alcoxi o C₃-C₆ grupos de cicloalquilo;

C₁-C₆ alcóxicarbonilo, C₃-C₆ cicloalquilcarbonilo, fenilo
opcionalmente sustituido con uno o más halógenos, C₁-C₄ alquilo o
C₁-C₄ grupos de alcoxi;

aminocarbonilo opcionalmente sustituido por uno o más grupos de
C₁-C₃- alquilo;

C₁-C₆ alcóxicarbonilo; C₁-C₆ alquilsulfonilo;

C₂-C₆ alquenilo; o NR₁₂R₁₃;

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m, p y q son cada uno un número entero de 1, 2, 3, 4, o 5;

n es un número entero de 0, 1 o 2;

r es un número entero de 1 hasta 2;

t es un número entero de 1, 2, 3, o 4;

R, R1, R2, R3, R4 y R5 son cada uno independientes de H o C1-C4 alquilo;

R6 es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C6 alcoxialquilo, C1-C6 alcoxi, C1-C6 haloalcoxi, C2-C6 alquenilo, C2-C6 alquenilo, C2-C6 alquinilo, C1-C6 alquilocarbonilo, C1-C6 alcoxicarbonilo, C1-C6 alquiltio, o C1-C6 haloalquiltio;

R7 y R8 son cada uno independientes de H; halógeno; C1-C6alquilo; C1-C6 alquilocarbonilo; o fenilo opcionalmente sustituido con uno o más halógenos, CN, NO₂, C1-C6alquilo, C2-C6 haloalquilo, C1-C6alcoxi o C1-C6 grupos de haloalcoxi;

R9 y R10 son cada uno independientes de H, o C1-C4alquilo;

R11 es H, C1-C6 alquilo, C1-C6 haloalquilo, C1-C4

alquilocarbonilo, C1-C6 alcoxicarbonilo o C1-C6

haloalcovicarbonilo;

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R12 y R13 son cada uno independientes de H o C1-C6 alquilo;
G es H; C1-C6 alquilo opcionalmente sustituido con uno o más
halógenos, C1-C4 alcoxi, C1-C6haloalcoxi, CN, NO₂S (O)uR14,
COR15, CO₂R16, fenilo o C3-C6 grupos de cicloalquilo;

C1-C6alcoxi; C1-C6 haloalcoxi; CN; NO₂; S(O)u R17; COR18;
CO₂R19; fenilo opcionalmente sustituido con uno o más halógenos,
CN, C1-C3 haloalquilo o C1-C3 grupos de haloalquilo;

C3-C6 cicloalquilo; Feniltio;

Q es fenilo opcionalmente sustituido con uno o más halógenos, CN,
SCN, NO₂, S(O)uR20, C1-C4 alquilo, C1-C4-haloalquilo, C1-C4
alcoxialquilo, C1-C6 alcoxi, C1-C6haloalcoxi, o grupos de
NR21R22;

R14, R15, R16, R18, R19, R21 y R22 son cada uno independientes
de H o C1-C6 alquilo;

R17 y R20 son cada uno independientes de C1-C6 alquilo o C1-C6
haloalquilo;

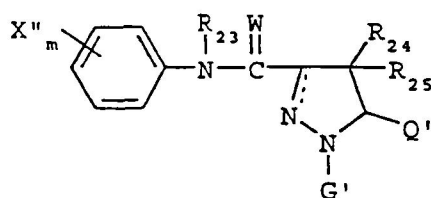
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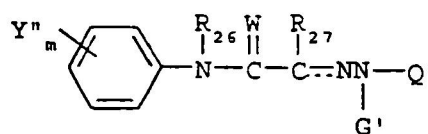
R33 es CO2R34;

R34 es H, C1-C6 alquilo, C1-C6 haloalquilo, fenilo o halofenilo; y la configuración de la línea de puntos C-.N representa un doble enlace o un enlace único; o un estereoisómero del mismo.

17. Un método de acuerdo a la reivindicación 15 la cual tiene un compuesto de un canal de sodio antagonista de la formula:



(IV)



(V)

en el cual W es O u S;

X' y Y' son independientes de H; halógeno; CN; SCN; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, NO2, CN, C1-C4 alcoxi, C1-C4 alquiltio, fenilo, halofenilo, C1-C4 alquilosulfonilo, C1-C4 haloalquilosulfonilo o C1-C4 grupos de alcoxycarbonilo;

C2-C4 alquenilo, C2-C4 haloalquenilo, C2-C4 alquinilo; C2-C4 haloalquinilo; C3-C6 cicloalquilo; C3-C6 halocicloalquilo; fenilo opcionalmente sustituido con uno o mas halógenos, CN, NO2, C1-C4

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alquilo, C1-C4 haloalquilo, C1-C4alcoxi, C1-C4 haloalcoxi, C1-C4
alquiltio, C1-C4 alquilosulfonilo o grupos de C1-C4
haloalquilosulfonilo;

C1- C4 alquilocarbonilo; C1-C4 haloalquilocarbonilo; o NR28R29;

m es un número entero de 1, 2, 3, 4, o 5;

G' es fenilo opcionalmente sustituido con uno o más grupos los
cuales pueden ser iguales o diferentes seleccionados de X' ;

un anillo heteroaromatico de 5 miembros que contiene de uno
a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1
azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo
heteroaromatico de 5 miembros el cual se encuentra unido por
medio del carbono y este puede ser opcionalmente sustituido
con uno o más grupos, los cuales pueden ser iguales o
diferentes, seleccionados de X'; o

un anillo heteroaromatico de 6 miembros que contiene de uno
a dos heteroatomos seleccionados de 0 o 1 oxígeno, 0 o 1
azufre y 0, 1 o 2 átomos de nitrógeno dichos anillo
heteroaromatico de 6 miembros el cual se encuentra unido

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por medio del carbono y este puede ser opcionalmente sustituido con uno o más grupos, los cuales pueden ser iguales o diferentes, seleccionados de X';

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Q es H; C1-C6 alquilo opcionalmente sustituido con uno o más halógenos, CN, C1-C3 alcoxi, C1-C6 alcóxicarbonilo o fenilo opcionalmente sustituido con uno o más halógenos, CN, NO₂, C1-C4 alquilo, C1-C4 haloalquilo, C1-C4 alquilosulfonilo o grupos de C1-C4 alquilosulfinilo;

C2- C6 alquénilo; C2-C6 alquínilo; o fenilo opcionalmente sustituido con uno o hasta tres grupos, los cuales pueden ser iguales o diferentes, seleccionados de X' ;

R23, R24, R25, R26, R27, R28 y R29 son cada uno independientes de H o C1-C4 alquilo; y la configuración de la línea de puntos C.-.N representa un enlace doble o un enlace sencillo; o un estereoisómero del mismo.

18. El método de acuerdo a la reivindicación 16 en la cual el canal neuronal de sodio antagonista es un compuesto de la fórmula I o III.

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19. El método de acuerdo a la reivindicación 18 en la cual la configuración de la línea de puntos representa un doble enlace.

20. Un método de acuerdo a la reivindicación 19 en la cual la fórmula III del compuesto se encuentra en la forma S.

21. El método de acuerdo a la reivindicación 20 en la cual W es O; X es trifluorometoxi y se encuentra en la 4 posición; Y es trifluorometoxi y se encuentra en la 3 -posición; Z es CN y se encuentra en la 4-posición; A es CH₂; n es 0; m, p y q son cada uno independientes de 1; R y R₁ son cada uno independientes de H; Z' es Cl; R₃₃ y G son cada uno independientes de CO₂CH₃; y Q es p-(trifluorometoxi) fenilo.

22. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del grupo A son cipermetrina, cihalometrina, ciflutrin, permetrin, etofenprox o silafluofen.

23. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del Grupo A son profenofos, acefato, sulprofos, malation, diazinon, metilo paration o terbufos.

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24. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del grupo A son metonilo, tiodicarbo o fenotiocarbo.

25. La composición de acuerdo a la reivindicación 21 en la cual uno o más compuestos seleccionados del grupo A son amitraz, clorodimeform o clorofenamidina.

26. La composición de acuerdo a la reivindicación 21 en la cual el o los compuestos seleccionados del grupo A son avermectina, anamectina, milbemectina, nemadectina, o moxidectina.

27. La composición de acuerdo a la reivindicación 21 en la cual el o los compuestos seleccionados del grupo A son hidrametilnon.

28. La composición de acuerdo a la reivindicación 21 en la cual el o los compuestos seleccionados del grupo A son fipronil, endosulfon, imidacloprid, acetamiprid, nitenpiram o tiametoxam.

29. Un método para proteger las plantas de ataques de insectos la cual consiste en aplicar al follaje de dicha planta una cantidad

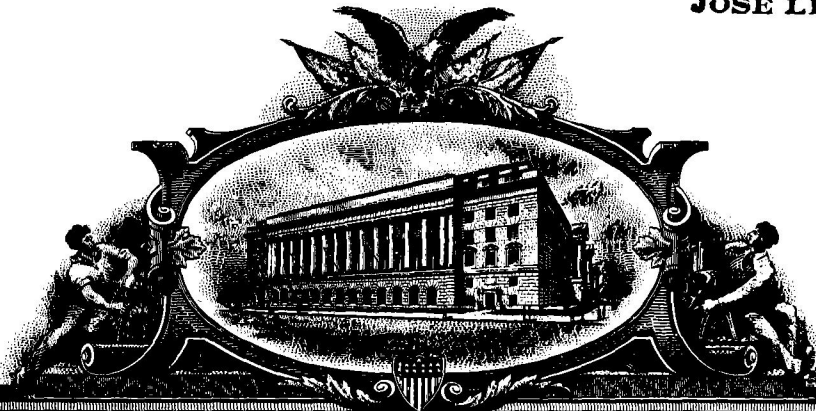
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sinérgicamente eficaz de la composición de acuerdo a la reivindicación 1.

30. El método de acuerdo a la reivindicación 29 en la cual los insectos son lepidoptera o coleoptera.

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THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

March 28, 2000

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

APPLICATION NUMBER: 60/158,201 ✓

FILING DATE: *October 07, 1999*



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

**P. SWAIN
Certifying Officer**

Assistant Commissioner for Patents
Washington, D.C. 20231

PROVISIONAL APPLICATION COVER SHEET

Transmitted herewith for filing under 37 CFR 1.53(c) is the provisional patent application of the following Inventor(s): Michael Frank Treacy, Paul E. Rensner, Raymond Frank Borysewicz, Hassan Oloume, Kurt Allen Schwinghammer;
For: SYNERGISTIC INSECTICIDAL COMPOSITIONS

1. Papers enclosed which are required for filing date under 37 CFR 1.51(c) and 1.53 (c):
 - 16 Pages of specification
 - 12 Pages of claims
 - 1 Page(s) of abstract
 - Sheets of drawing
 - ☐ Formal
 - ☐ Informal
2. Inventor(s) name(s) and address(es) (or list attorney docket number as alphanumeric identifier):

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Hamilton Square, NJ 08690	Yardley, PA 19067
 Kurt Allen Schwinghammer	
1206 University Drive	
Yardley, PA 19067	
3. Assignment
An assignment of the invention to:
American Cyanamid Company
5 Giralda Farms
Madison, New Jersey 07940-0874

- ☐ was made in the prior application and recorded in PTO on _____, Reel _____, Frame _____
- ☐ is attached under separate Recordation Form Cover Sheet.
- ☐ will follow.

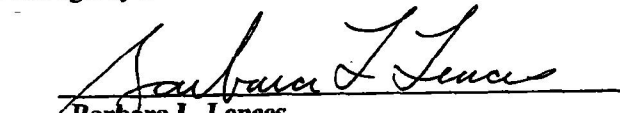
CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that this paper and the documents referred to as enclosed therein are being deposited with the United States Postal Service on the date written below in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number TB13073433XUS addressed to the Assistant Commissioner for Patents, Box Provisional Patent Application, Washington, D.C. 20231.

Oct 7, 1999
Date

Barbara L. Lences
Barbara L. Lences

4. Filing Fee \$150.00
5. Method of Payment of Fees:
Charge Deposit Account No. 01-1300 in the amount of \$ 150.00
A duplicate of this transmittal is attached.
6. Instructions as to Overpayment:
Credit any overpayment to Deposit Account No. 01-1300.
7. Authorization to Charge Additional Fees
☒ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Deposit Account No. 01-1300:
☒ 37 CFR 1.51(a)(2) and 1.53 (c) filing fees
☒ Surcharge for filing the basic filing fee and/or complete cover sheet on a date later than the filing date of the application.
8. Attorney/Agent Names/Registration Nos.
- | | | |
|----------------------|----------|--------|
| John W. Hogan, Jr. | Reg. No. | 32,703 |
| William H. Calnan | Reg. No. | 29,520 |
| Gregory M. Hill | Reg. No. | 31369 |
| Charles F. Costello | Reg. No. | 27,324 |
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Tel. No. (973) 683-2152
10. The invention was made by an agency of the U.S. Government or under a contract with an agency of the U.S. Government.
☒ No
☐ Yes, the name of the U.S. Government agency and the Government contract numbers are _____


Barbara L. Lences

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33562-01L

SYNERGISTIC INSECTICIDAL COMPOSITIONS

BACKGROUND OF THE INVENTION

1 Insecticidal agents and compositions have been
2 developed to control insect pests such as
3 agrohorticultural pests, hygienic pests, or wood-eating
4 pests and in practice have been used as a single or a
5 mixed agent. However, economically efficient and
6 ecologically safe insect control compositions are still
7 being sought. Insecticidal compositions which allow for
8 reduced effective dosage rates, increased environmental
9 safety and lower incidence of insect resistance are
10 highly desirable. Although the rotational application of
11 insect control agents having different modes of action
12 may be adopted for good pest management practice, this
13 approach does not necessarily give satisfactory insect
14 control. Further, eventhough combinations of insect
15 control agents have been studied, a high synergistic
16 action has not always been found. Obtaining an
17 insecticidal composition which demonstrates no cross-
18 resistance to existing insecticidal agents, no toxicity
19 problems and little negative impact on the environment is
20 extremely difficult.

21 Therefore, it is an object of this invention to provide
22 a synergistic insecticidal composition which demonstrates a
23 high controlling effect with concomittant reduced crop
24 production cost and reduced environmental load.

25 It is another object of this invention to provide
26 methods for synergistic insect control and enhanced crop
27 protection.

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28 SUMMARY OF THE INVENTION

29 The present invention provides a synergistic
30 insecticidal composition comprising as essential active
31 ingredients a synergistically effective amount of a
32 neuronal sodium channel antagonist in combination with
33 one or more compounds selected from the group consisting
34 of pyrethroids, pyrethroid-type compounds,
35 organophosphates, carbamates, formamidines, macrocyclic
36 lactones, amidinohydrazones, GABA (gamma-aminobutyric
37 acid) antagonists, and acetylcholine receptor ligands.

38 The present invention also provides a method for
39 synergistic insect control which comprises contacting
40 said insect with a synergistically effective amount of a
41 neuronal sodium channel antagonist in combination with
42 one or more compounds selected from the group consisting
43 of pyrethroids, pyrethroid-type compounds,
44 organophosphates, carbamates, formamidines, macrocyclic
45 lactones, amidinohydrazones, GABA antagonists and
46 acetylcholine receptor ligands.

47 The present invention further provides a method for
48 the enhanced protection of plants from infestation and
49 attack by insects.

50

51

52 DETAILED DESCRIPTION OF THE INVENTION53 Definitions

54 "Acetylcholine receptor ligand compound" as used in
55 this application means a compound which is capable of
56 binding to the acetylcholine receptor site.

57 "Group A" as used in this application means
58 insecticidal

- 59 1) pyrethroid compounds;
60 2) pyrethroid-type compounds;
61 3) organophosphate compounds;
62 4) carbamate compounds;
63 5) formamidine compounds;

- 64 6) macrocyclic lactone compounds;
65 7) amidinohydrazone compounds;
66 8) GABA antagonist compounds; and
67 9) acetylcholine receptor ligand compounds.

68 "Haloalkyl" as used in this application means an
69 alkyl group C_xH_{2x+1} having 1 to $2x+1$ halogen atoms which may
70 be the same or different. Similarly, the terms
71 "haloalkenyl", "haloalkynyl", "haloalkoxy", "halophenyl"
72 and the like mean mono- to perhalogen substitution
73 wherein the halogens may be the same or different.

74 "Halogen" as used in this application means Cl, Br, I
75 or F.

76 "Neuronal sodium channel antagonist" as used in this
77 application means a compound which is capable of
78 preventing the ability of a neuron cell to transfer sodium
79 ions across the cell membrane.

80 "Pyrethroid-type compounds" as used in this
81 application means those compounds characterized by a non-
82 ester linked aryl-phenoxybenzyl moiety.

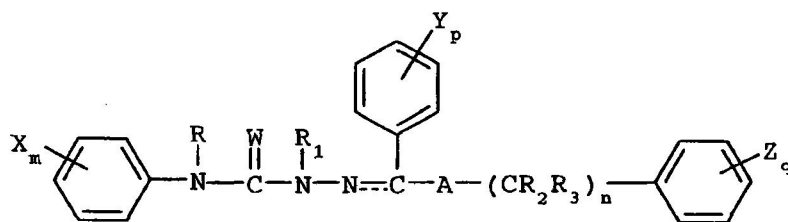
83 "Synergism" as used in this application means a
84 cooperative action encountered in a combination of two or
85 more biologically active components in which the combined
86 activity of the two or more components exceeds the sum of
87 the activity of each component alone.

88
89 Surprisingly, it has now been found that a
90 composition which comprises a combination of a neuronal
91 sodium channel antagonist and a second insecticidal
92 ingredient provides superior insect control at lower
93 levels of the combined active agents than may be achieved
94 when the neuronal sodium channel antagonist or the second
95 insecticidal ingredient is applied alone.

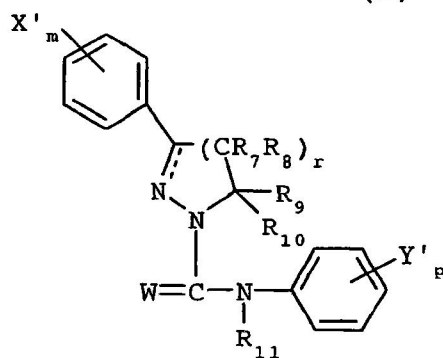
96 As previously stated, the term neuronal sodium
97 channel antagonist designates a compound which is capable
98 of preventing the ability of a neuron cell to transfer

99 sodium ions across the cell membrane. A neuron cell thus
 100 affected is unable to fire, resulting in paralysis, and
 101 ultimately mortality, in the target host. Descriptions
 102 of neuronal sodium channel antagonists and their mode of
 103 action may be found in Pesticide Biochemistry and
 104 Physiology, 60: 177-185 or Archives of Insect
 105 Biochemistry and Physiology, 37: 91-103.

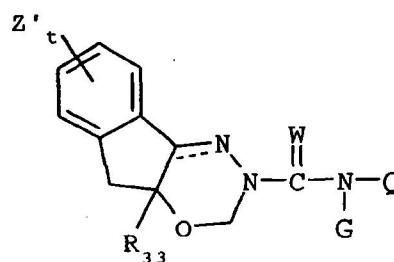
106 Neuronal sodium channel antagonists include
 107 compounds such as those described in U.S. 5,543,573; U.S.
 108 5,708,170; U.S. 5,324,837 and U.S. 5,462,938, among other
 109 publications. Exemplary of the neuronal sodium channel
 110 antagonist compounds useful in the composition of this
 111 invention are those compounds having the structural
 112 formula
 113



(I)



(II)



(III)

117 wherein A is CR₄R₅ or NR₆;

118 W is O or S;

119 X, Y, Z, X', Y' and Z' are each independently H;

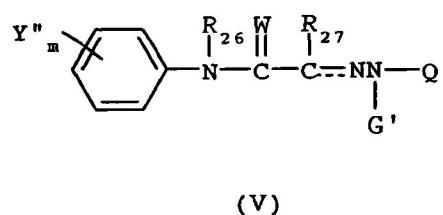
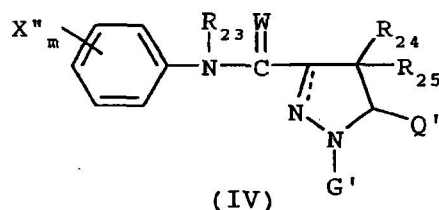
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120 halogen; OH; CN; NO₂; C₁-C₆alkyl optionally
121 substituted with one or more halogen, C₁-
122 C₃alkoxy, C₁-C₃haloalkoxy, C₃-C₆cycloalkyl,
123 C₂-C₆alkenyloxy or sulfonyloxy groups;
124 C₁-C₆alkoxy optionally substituted with one or
125 more halogen, C₁-C₃alkoxy or C₃-C₆cycloalkyl
126 groups;
127 C₁-C₆alkoxycarbonyl, C₃-C₆cycloalkylcarbonyloxy,
128 phenyl optionally substituted with one or
129 more halogen, C₁-C₆alkyl, or C₁-C₆alkoxy
130 groups;
131 aminocarbonyloxy optionally substituted with
132 one or more C₁-C₃alkyl groups;
133 C₁-C₆alkoxycarbonyloxy; C₁-C₆alkylsulfonyloxy; C₂-
134 C₆alkenyl; or NR₁₂R₁₃;
135 m, p and q are each independently an integer of 1,
136 2, 3, 4, or 5;
137 n is an integer of 0, 1 or 2;
138 r is an integer of 1 or 2;
139 t is an integer of 1, 2, 3 or 4;
140 R, R₁, R₂, R₃, R₄ and R₅ are each independently H or
141 C₁-C₆alkyl;
142 R₆ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxyalkyl,
143 C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyl, C₂-
144 C₆alkynyl, C₁-C₆alkylcarbonyl, C₁-C₆alkoxy-
145 carbonyl, C₁-C₆alkylthio, or C₁-C₆haloalkylthio;
146 R₇ and R₈ are each independently H; halogen; C₁-
147 C₆alkyl; C₁-C₆alkylcarbonyloxy; or phenyl
148 optionally substituted with one or more
149 halogen, CN, NO₂, C₁-C₆alkyl, C₂-C₆haloalkyl,
150 C₁-C₆alkoxy or C₁-C₆haloalkoxy groups;
151 R₉ and R₁₀ are each independently H, or C₁-C₆alkyl;
152 R₁₁ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-
153 C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, or C₁-
154 C₆haloalkoxycarbonyl;

155 R_{12} and R_{13} are each independently H or C_1 - C_6 alkyl;
156 G is H; C_1 - C_6 alkyl optionally substituted with one or
157 more halogen, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy,
158 CN, $NO_2S(O)_uR_{14}$, COR_{15} , CO_2R_{16} , phenyl or C_1 -
159 C_6 cycloalkyl groups;
160 C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; CN; NO_2 ; $S(O)_uR_{17}$;
161 COR_{18} ; CO_2R_{19} ; phenyl optionally substituted
162 with one or more halogen, CN, C_1 - C_3 halo-
163 alkyl, or C_1 - C_3 haloalkoxy groups;
164 C_3 - C_6 cycloalkyl; or phenylthio;
165 Q is phenyl optionally substituted with one or more
166 halogen, CN, SCN, NO_2 , $S(O)_uR_{20}$, C_1 - C_6 alkyl, C_1 -
167 C_6 haloalkyl, C_1 - C_6 alkoxyalkyl, C_1 - C_6 alkoxy, C_1 -
168 C_6 haloalkoxy, or $NR_{21}R_{22}$ groups;
169 u is an integer of 0, 1 or 2;
170 R_{14} , R_{15} , R_{16} , R_{18} , R_{19} , R_{21} and R_{22} are each independently
171 H or C_1 - C_6 alkyl;
172 R_{17} and R_{20} are each independently C_1 - C_6 alkyl or
173 C_1 - C_6 haloalkyl;
174 R_{33} is CO_2R_{34} ;
175 R_{34} is H, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, phenyl or
176 halophenyl; and the dotted line configuration
177 $C \equiv N$ represents a double bond or a single bond (i.e.
178 C-N or C=N); or
179 a stereoisomer thereof.
180 Preferred neuronal sodium channel antagonists suitable
181 for use in the composition of the invention are those
182 compounds of formula I, II or III wherein the dotted line
183 configuration $C \equiv N$ represents a double bond.
184 More preferred neuronal sodium channel antagonists
185 suitable for use in the inventive composition are those
186 compounds of formula I or formula III wherein the dotted
187 line configuration represents a double bond.
188 Particularly preferred neuronal sodium channel
189 antagonists useful in the composition of the invention

are those compounds of formula I or formula III wherein W is O; X is trifluoromethoxy and is in the 4-position; Y is trifluoromethyl and is in the 3-position; Z is CN and is in the 4-position; A is CH₃; n is 0; m, p and q are each 1; R and R₁ are each H; Z' is Cl; R₃ and G are each CO₂CH₃; Q is *p*-(trifluoromethoxy)phenyl; and the dotted line configuration C=N represents a double bond; or a stereoisomer thereof.

Further neuronal sodium channel antagonist compounds include those described in U.S. 5,116,850 and U.S. 5,304,573, among other publications. Exemplary of further neuronal sodium channel antagonist compounds suitable for use in the composition of the invention are those compounds having structural formula



205
206

wherein W is O or S;

X' and Y' are each independently H; halogen; CN; SCN;
C₁-C₆alkyl optionally substituted with one or more halogen, NO₂, CN, C₁-C₄alkoxy, C₁-C₄alkylthio, phenyl, halophenyl, C₁-C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl, or C₁-C₄alkoxycarbonyl groups;
C₂-C₄alkenyl; C₂-C₄haloalkenyl; C₂-C₄alkynyl; C₂-C₄haloalkynyl; C₃-C₆cycloalkyl; C₃-C₆halocycloalkyl; phenyl optionally substituted with one or more halogen, CN, NO₂, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, C₁-C₄alkylsulfonyl or C₁-C₄haloalkylsulfonyl groups;

A3
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221 C₁-C₆alkylcarbonyl; C₁-C₆haloalkylcarbonyl; or
222 NR₂₈R₂₉;
223 m is an integer of 1, 2, 3, 4 or 5;
224 G' is phenyl optionally substituted with one or more
225 groups which may be the same or different
226 selected from X';
227 a 5-membered heteroaromatic ring containing one
228 or two heteroatoms selected from 0 or 1
229 oxygen, 0 or 1 sulfur and 0, 1 or 2
230 nitrogen atoms said 5-membered
231 heteroaromatic ring being attached via
232 carbon and being optionally substituted
233 with one or more groups which may be the
234 same or different selected from X'; or
235 a 6-membered heteroaromatic ring containing one
236 or two heteroatoms selected from 0 or 1
237 oxygen, 0 or 1 sulfur and 0, 1 or 2
238 nitrogen atoms said 6-membered
239 heteroaromatic ring being attached via
240 carbon and being optionally substituted
241 with one or more groups which may be the
242 same or different selected from X';
243 Q' is H; C₁-C₆alkyl optionally substituted with one or
244 more halogen, CN, C₁-C₃alkoxy, C₁-
245 C₆alkoxycarbonyl, or phenyl optionally
246 substituted with one or more halogen,
247 CN, NO₂, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-
248 C₆alkylsulfonyl or C₁-C₆alkylsulfinyl
249 groups;
250 C₂-C₆alkenyl; C₂-C₆alkynyl; or phenyl optionally
251 substituted with one to three groups,
252 which may be the same or different,
253 selected from X';
254 R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈ and R₂₉ are each
255 independently H or C₁-C₆alkyl; and the dotted

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141

256 line configuration $C \equiv N$ represents a double bond or
257 a single bond (i.e. C-N or C=N); or
258 a stereoisomer thereof.

259 Further preferred neuronal sodium channel antagonist
260 compounds of the invention are those compounds of formula
261 IV or V wherein the dotted line configuration $C \equiv N$
262 represents a double bond.

263 Other preferred neuronal sodium channel antagonist
264 compounds suitable for use in the composition of the
265 invention are those compounds of formula IV or V wherein
266 W is O; X" and Y" are each independently H or C₁-
267 C₆haloalkyl; m is 1; R₂₃, R₂₄, R₂₅, R₂₆ and R₂₇ are each H; G
268 is phenyl optionally substituted with one or more halogen
269 atoms; Q' is halophenyl or C₁-C₆alkyl optionally
270 substituted with one phenyl or halophenyl group; and the
271 dotted line configuration $C \equiv N$ represents a double bond;
272 or a stereoisomer thereof.

273 The second active ingredient of the insecticidal
274 composition of the invention includes one or more
275 compounds selected from Group A:

276 1) pyrethroid compounds which are known to be
277 insecticidally active such as cypermethrin, cyhalothrin,
278 cyfluthrin, permethrin or the like;

279 2) pyrethroid-type compounds which are known to be
280 insecticidally active such as ethofenprox, silafluofen,
281 or the like;

282 3) organophosphate compounds which are known to be
283 insecticidally active such as profenofos, acephate,
284 sulprofos, malathion, diazinon, methyl parathion,
285 terbufos, or the like;

286 4) carbamate compounds which are known to be
287 insecticidally active such as methomyl, thiodicarb,
288 fenothiocarb, or the like;

289 5) formamidine compounds which are known to be
290 insecticidally active such as amitraz, chlordimeform,
291 hydramethylnon, chlorfenamidin, or the like;

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292 6) macrocyclic lactone compounds which are known
293 to be insecticidally active such as spinosad, avermectin,
294 emamectin, milbemectin, nemadectin, moxidectin or the
295 like;

296 7) amidinohydrazone compounds which are known to
297 be insecticidally active such as hydramethylnon;

298 8) GABA antagonist compounds which are known to be
299 insecticidally effective such as fipronil, endosulfan, or
300 the like;

301 9) acetylcholine receptor ligand compounds which
302 are known to be insecticidally effective such as
303 imidacloprid, acetamiprid, nitenpyram, thiamethoxam, or
304 the like.

305 Descriptions of the above-listed commercially
306 available compounds may be found in The Pesticide Manual,
307 11th Edition, British Crop Protection Council (1997) among
308 other publications.

309 Preferred compositions of the invention are those
310 compositions having a neuronal sodium channel antagonist
311 compound of formula I or formula III in combination with
312 one or more compounds selected from Group A.

313 More preferred compositions of the invention are those
314 compositions having a formula I or formula III compound
315 wherein W is O; X is trifluoromethoxy and is in the 4-
316 position; Y is trifluoromethyl and is in the 3-position; Z
317 is CN and is in the 4-position; A is CH₃; n is 0; m, p and
318 q are each independently 1; R and R₁ are each independently
319 H; Z' is Cl; R₂ and G are each independently CO₂CH₃; Q is
320 p-(trifluoromethoxy)phenyl; and the dotted line
321 configuration C=N represents a double bond in combination
322 with one or more compounds selected from Group A.

323 Each of the compounds of formula I, II, III, IV and
324 V embody assymetric centers which may be represented in
325 the stereoisomeric R-form or S-form. The present
326 invention also includes the R-form, the S-form or

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327 mixtures comprising the R-form and the S-form in an
328 arbitrary ratio. For compounds of formula III, the S-
329 form is preferred.

330 Advantageously, the neuronal sodium-channel antagonist
331 compound of formula I, II, III, IV or V or a mixture
332 thereof may be formulated with a second insecticidally
333 effective ingredient and optionally other customary
334 formulation adjuvants. Said formulation may be dispersed
335 in a solid or liquid diluent for application to the insect,
336 its food supply, breeding ground or habitat as a dilute
337 spray or as a solid dust or dust concentrate.

338 The active ingredients of the inventive composition
339 may also be formulated separately as a wettable powder,
340 emulsifiable concentrate, aqueous or liquid flowable,
341 suspension concentrate or any one of the conventional
342 formulations used for insect control agents and tank-
343 mixed in the field with water or other inexpensive liquid
344 for application as a liquid spray mixture. The
345 separately formulated compositions may also be applied
346 sequentially.

347 Advantageously, the composition of the invention may
348 be formulated as a bait composition comprising a
349 synergistically effective amount of a combination of a
350 neuronal sodium channel antagonist plus one or more
351 compounds selected from Group A and a solid or liquid
352 edible nutritive substance. A preferred bait composition
353 may contain by weight about 0.01% to 20% active
354 ingredients, preferably a neuronal sodium channel
355 antagonist in combination with hydramethylnon.

356 In actual practice, the composition of the invention
357 is applied to the plant foliage or plant stem or insect
358 habitat as a dilute spray prepared from any of the above-
359 said formulations. The ratio of the essential active
360 ingredients of the composition of the invention is about
361 1 weight part of a neuronal sodium channel antagonist to

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362 about 0.01-100 weight parts of one or more compounds
363 selected from Group A.

364 The compositions of the invention are superior
365 insecticidal compositions and are especially useful for
366 protecting growing and harvested plants including:
367 leguminous crops such as soybeans, snap beans, peas, wax
368 beans and the like as well as cotton, forage crops, cole
369 crops, leafy vegetables, tobacco, hops, tomatoes,
370 potatoes, flowering ornamentals such as chrysanthemums,
371 vine crops such as grapes, squash, pumpkin or melon and
372 fruit trees such as cherry, peach, apple or citrus, from
373 the ravages of insects.

374 The synergistic insecticidal composition of the
375 invention is found to be highly active against a wide
376 variety of lepidopteran and coleopteran insects such as
377 *Helicoverpa zea* (cotton bollworm), *Heliothis virescens*
378 (tobacco budworm), *Leptinotarsa decemlineata* (Colorado potato
379 beetle), *Diabrotica spp.* (corn rootworm) and the like.

380 Also the composition of the invention may be useful
381 for the prevention and control of public health pests
382 such as houseflies, mosquitoes, cockroaches, ants,
383 termites or the like.

384 Further, the compositions of the invention may be
385 particularly useful for the prevention and control of
386 wood-eating insects such as termites, carpenter ants,
387 wood-destroying beetles or the like.

388 These and other advantages of the invention may become
389 more apparent from the examples set forth herein below.
390 These examples are provided merely as illustrations of the
391 invention and are not intended to be construed as a
392 limitation thereof.

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145EXAMPLE 1

Evaluation of the Synergistic Insecticidal Effect of
a Combination of a Neuronal Sodium Channel Antagonist
Plus a Second Insecticide

In this evaluation, *Heliothis zea* (cotton bollworm),
Heliothis virescens (tobacco budworm) and pyrethroid-
resistant *Heliothis virescens* larvae used are obtained
from laboratory colonies. Pyrethroid-resistant *H.*
virescens are derived from the PEG-strain [Campannola &
Plapp, Proceedings of Beltwide Cotton Conference (1988)].

Cotton leaves are immersed in 1:1 v/v, acetone/water
solutions of test compound, or solutions of a combination
of test compounds for a period of about 3 seconds.
Following immersion, leaves are allowed to air-dry for 2-3
hours. Plastic bioassay trays containing multiple open-
faced wells (4.0 x 4.0 x 2.5 cm) are used as the test
arenas. Cut portions of a treated leaf, a moistened
cotton dental wick and a single third-instar larva are
placed into each well, covered with an adhesive vented
clear plastic sheet and held under constant fluorescent
light at about 27°C for a predetermined period of time.
Larval mortality/morbidity is evaluated at 5 days after
treatment. All treatments are replicated 4-5 fold in a
randomized complete block design with 16-32 larvae per
treatment. Using conventional log-probit analysis, the
LC₅₀ of each treatment is determined.

Using the above protocol, a neuronal sodium channel
antagonist (Compound A) is evaluated alone at dose rates
of 0.1 ppm, 1.0 ppm and 10.0 ppm and in combination with
1.0 ppm of a second insecticidal compound. The treatments
used are shown in Table I.

Each of the combinations evaluated demonstrates
synergistic insecticidal activity.

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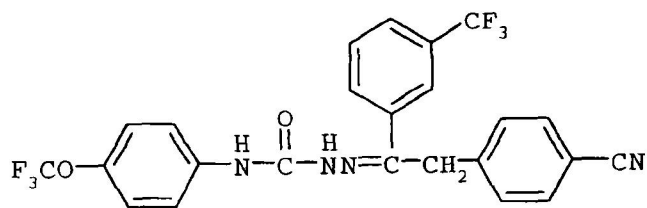
Table I

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Second Active Compound	Dose Rate (ppm)	Compound A ¹			
		Dose Rate			
		(ppm)	(ppm)	(ppm)	(ppm)
cypermethrin	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
amitraz	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
fipronil	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
acetamiprid	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
spinosad	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0
thiodicarb	0	0	0.1	1.0	10.0
	1.0	0	0.1	1.0	10.0

¹Compound A = formula Ia neuronal sodium channel antagonist

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(Ia)

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EXAMPLE 2

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Evaluation of the Synergistic Insecticidal Effect Of
a Combination Of A Neuronal Sodium Channel Antagonist
Plus an Amidinohydrazone

In this evaluation, adult male German cockroaches (*Blattella germanica*) are used. For each test, a 4.0 g portion of ground Purina Dog Chow (Hi-Pro Glo®) is treated with an acetone solution of test compound alone or in combination with a second test compound. After treatment, the acetone is evaporated and the treated dog chow is placed in a 3/4 oz plastic cup which is placed in a harborage made of folded sheets of blotter paper placed in a plastic box (16"L x 11"W x 6"H). The plastic box (test arena) is also fitted with a 1 oz narrow mouth bottle with 2 dental wicks inserted at the mouth. A control box is prepared in the same manner using ground dog chow which has been treated with reagent grade acetone. Each treatment is replicated three times. Into each test arena are placed 20 healthy adult male cockroaches which have been reared in an insectary. The test arenas are then stored at 76°F and mortality is determined daily by visual examination. The data obtained are shown in Table II.

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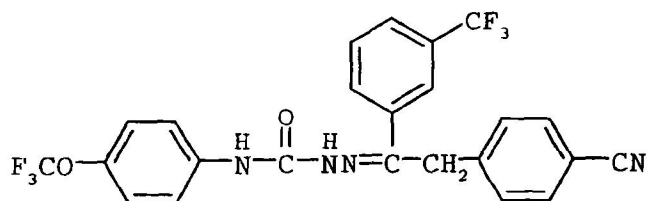
Table II

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Test	% Active	% Mortality					
		Days After Treatment					
<u>Compound</u>	<u>Ingredient</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
A ¹	0.05	0	0	0	0	0	0
A	0.10	1.7	11.7	11.7	11.7	18.3	18.3
A	0.50	5.0	5.0	5.0	5.0	5.0	5.0
B ²	1.00	0	5.0	28.3	71.7	90.0	93.3
A+B	0.05+1.0	0	20.0	41.7	81.7	95.0	98.3
A+B	0.10+1.0	0	21.7	51.7	88.3	95.0	95.0
A+B	0.50+1.0	16.7	58.3	80.0	95.0	98.3	100.0
Control	0	0	1.7	3.3	3.3	3.3	5.0

¹Compound A = formula Ia neuronal sodium channel antagonist²Compound B = hydramethylnon

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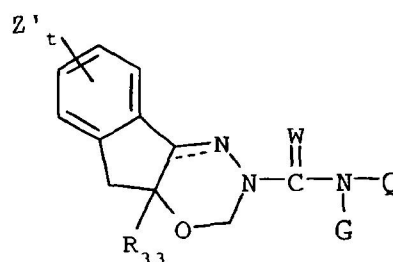
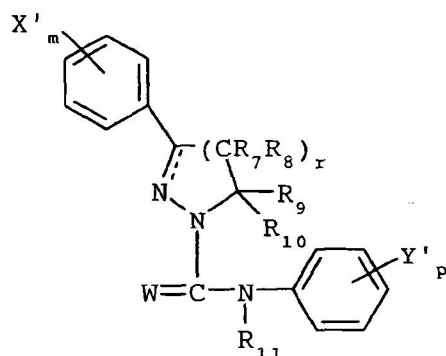
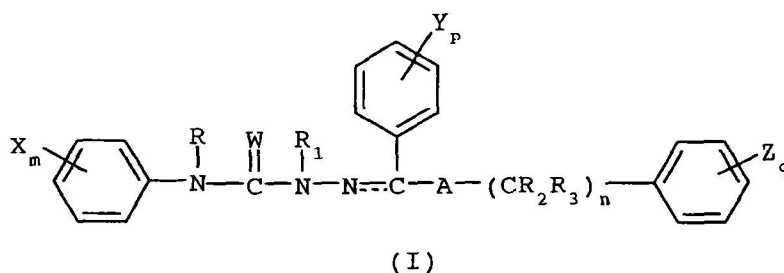
As can be seen from the data shown in Table II, combinations of a neuronal sodium channel antagonist plus an amidinohydrazone insecticide demonstrate synergistic insect control.

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WHAT IS CLAIMED IS:

- 1 1. A synergistic insecticidal composition
 2 comprising a synergistically effective amount of a
 3 neuronal sodium channel antagonist in combination with
 4 one or more compounds selected from Group A.

- 1 2. The composition according to claim 1 having a
 2 neuronal sodium channel antagonist compound of formula
 3



- 6
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 9 wherein A is CR_4R_5 or NR_6 ;
 10 W is O or S;
 11 X, Y, Z, X', Y' and Z' are each independently H;
 12 halogen; OH; CN; NO₂; C₁-C₆alkyl optionally

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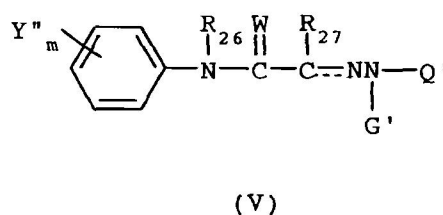
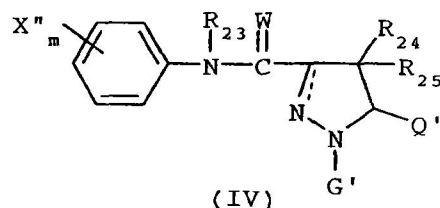
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1 substituted with one or more halogen, C₁-
2 C₃alkoxy, C₁-C₃haloalkoxy, C₃-C₆cycloalkyl,
3 C₂-C₆alkenyloxy or sulfonyloxy groups;
4 C₁-C₆alkoxy optionally substituted with one or
5 more halogen, C₁-C₃alkoxy or C₃-C₆cycloalkyl
6 groups;
7 C₁-C₆alkoxycarbonyl, C₃-C₆cycloalkylcarbonyloxy,
8 phenyl optionally substituted with one or
9 more halogen, C₁-C₄alkyl, or C₁-C₄alkoxy
10 groups;
11 aminocarbonyloxy optionally substituted with
12 one or more C₁-C₃alkyl groups;
13 C₁-C₆alkoxycarbonyloxy; C₁-C₆alkylsulfonyloxy; C₂-
14 C₆alkenyl; or NR₁₂R₁₃;
15 m, p and q are each independently an integer of 1,
16 2, 3, 4, or 5;
17 n is an integer of 0, 1 or 2;
18 r is an integer of 1 or 2;
19 t is an integer of 1, 2, 3 or 4;
20 R, R₁, R₂, R₃, R₄ and R₅ are each independently H or
21 C₁-C₄alkyl;
22 R₆ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkoxyalkyl,
23 C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyl, C₂-
24 C₆alkynyl, C₁-C₆alkylcarbonyl, C₁-C₆alkoxy-
25 carbonyl, C₁-C₆alkylthio, or C₁-C₆haloalkylthio;
26 R₇ and R₈ are each independently H; halogen; C₁-
27 C₆alkyl; C₁-C₆alkylcarbonyloxy; or phenyl
28 optionally substituted with one or more
29 halogen, CN, NO₂, C₁-C₆alkyl, C₂-C₆haloalkyl,
30 C₁-C₆alkoxy or C₁-C₆haloalkoxy groups;
31 R₉ and R₁₀ are each independently H, or C₁-C₄alkyl;
32 R₁₁ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-
33 C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, or C₁-
34 C₆haloalkoxycarbonyl;
35 R₁₂ and R₁₃ are each independently H or C₁-C₆alkyl;

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36 G is H; C₁-C₆alkyl optionally substituted with one or
 37 more halogen, C₁-C₆alkoxy, C₁-C₆haloalkoxy,
 38 CN, NO₂S(O)_uR₁₄, COR₁₅, CO₂R₁₆, phenyl or C₃-
 39 C₆cycloalkyl groups;
 40 C₁-C₆alkoxy; C₁-C₆haloalkoxy; CN; NO₂; S(O)_uR₁₇;
 41 COR₁₈; CO₂R₁₉; phenyl optionally substituted
 42 with one or more halogen, CN, C₁-C₃halo-
 43 alkyl, or C₁-C₃haloalkoxy groups;
 44 C₃-C₆cycloalkyl; or phenylthio;
 45 Q is phenyl optionally substituted with one or more
 46 halogen, CN, SCN, NO₂, S(O)_uR₂₀, C₁-C₆alkyl, C₁-
 47 C₆haloalkyl, C₁-C₆alkoxyalkyl, C₁-C₆alkoxy, C₁-
 48 C₆haloalkoxy, or NR₂₁R₂₂ groups;
 49 u is an integer of 0, 1 or 2;
 50 R₁₄, R₁₅, R₁₆, R₁₈, R₁₉, R₂₁ and R₂₂ are each independently
 51 H or C₁-C₆alkyl;
 52 R₁₇ and R₂₀ are each independently C₁-C₆alkyl or
 53 C₁-C₆haloalkyl;
 54 R₃₃ is CO₂R₃₄;
 55 R₃₄ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, phenyl or
 56 halophenyl; and the dotted line configuration
 57 C=N represents a double bond or a single bond; or
 58 a stereoisomer thereof.

1 3. The composition according to claim 1
 2 having a neuronal sodium channel antagonist compound of
 3 formula



7 wherein W is O or S;
8 X' and Y' are each independently H; halogen; CN; SCN;
9 C₁-C₆alkyl optionally substituted with one or
10 more halogen, NO₂, CN, C₁-C₄alkoxy, C₁-
11 C₄alkylthio, phenyl, halophenyl, C₁-
12 C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl, or
13 C₁-C₄alkoxycarbonyl groups;
14 C₂-C₄alkenyl; C₂-C₄haloalkenyl; C₂-C₄alkynyl; C₂-
15 C₄haloalkynyl; C₃-C₆cycloalkyl; C₃-
16 C₆halocycloalkyl; phenyl optionally substituted
17 with one or more halogen, CN, NO₂, C₁-C₄alkyl,
18 C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy,
19 C₁-C₄alkylthio, C₁-C₄alkylsulfonyl or C₁-
20 C₄haloalkylsulfonyl groups;
21 C₁-C₄alkylcarbonyl; C₁-C₄haloalkylcarbonyl; or
22 NR₂₈R₂₉;
23 m is an integer of 1, 2, 3, 4 or 5;
24 G' is phenyl optionally substituted with one or more
25 groups which may be the same or different
26 selected from X';
27 a 5-membered heteroaromatic ring containing one
28 or two heteroatoms selected from 0 or 1
29 oxygen, 0 or 1 sulfur and 0, 1 or 2
30 nitrogen atoms said 5-membered
31 heteroaromatic ring being attached via
32 carbon and being optionally substituted
33 with one or more groups which may be the
34 same or different selected from X'; or
35 a 6-membered heteroaromatic ring containing one
36 or two heteroatoms selected from 0 or 1
37 oxygen, 0 or 1 sulfur and 0, 1 or 2
38 nitrogen atoms said 6-membered
39 heteroaromatic ring being attached via
40 carbon and being optionally substituted
41 with one or more groups which may be the

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42 same or different selected from X';
43 Q' is H; C₁-C₆alkyl optionally substituted with one or
44 more halogen, CN, C₁-C₃alkoxy, C₁-
45 C₆alkoxycarbonyl, or phenyl optionally
46 substituted with one or more halogen,
47 CN, NO₂, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-
48 C₄alkylsulfonyl or C₁-C₄alkylsulfinyl
49 groups;
50 C₂-C₆alkenyl; C₂-C₆alkynyl; or phenyl optionally
51 substituted with one to three groups,
52 which may be the same or different,
53 selected from X';
54 R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈ and R₂₉ are each
55 independently H or C₁-C₄alkyl; and the dotted
56 line configuration C=N represents a double bond or
57 a single bond; or
58 a stereoisomer thereof.

1 4. The composition according to claim 2 wherein
2 the neuronal sodium channel antagonist is a compound of
3 formula I or III.

1 5. The composition according to claim 4 wherein
2 the dotted line configuration C=N represents a double
3 bond.

1 6. The composition according to claim 5 wherein
2 the compound of formula III is in the S-form.

1 7. The composition according to claim 6 wherein W
2 is O; X is trifluoromethoxy and is in the 4-position; Y
3 is trifluoromethyl and is in the 3-position; Z is CN and
4 is in the 4-position; A is CH₃; n is 0; m, p and q are
5 each 1; R and R₁ are each H; Z' is Cl; R₃₃ and G are each
6 CO₂CH₃; and Q is p-(trifluoromethoxy)phenyl.

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1 8. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 cypermethrin, cyhalomethrin, cyfluthrin, permethrin,
4 ethofenprox or silafluofen.

1 9. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 profenofos, acephate, sulprofos, malathion, diazinon,
4 methyl parathion, or terbufos.

1 10. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 methonyl, thiodicarb, or fenothiocarb.

1 11. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 amitraz, chlordimeform, or chlorfenamidine.

1 12. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 avermectin, emamectin, milbemectin, nemadectin, or
4 moxidectin.

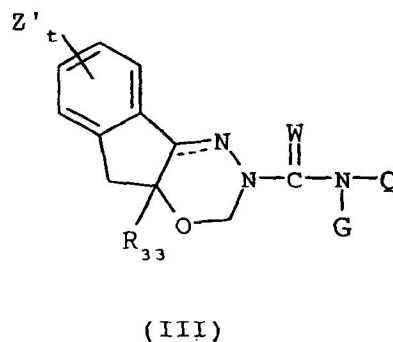
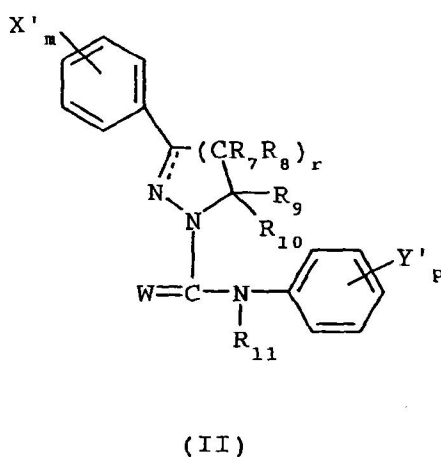
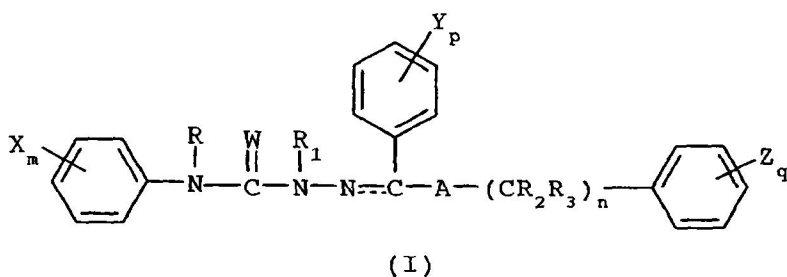
1 13. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A is
3 hydramethylnon.

1 14. The composition according to claim 7 wherein
2 the one or more compounds selected from Group A are
3 fipronil, endosulfon, imidacloprid, acetamiprid,
4 nitenpyram or thiamethoxam.

1 15. A method for synergistic insect control which
2 comprises contacting said insect with a synergistically

3 effective amount of a neuronal sodium channel antagonist
4 in combination with one or more compounds selected from
5 Group A.

1 16. The method according to claim 15 having a
2 neuronal sodium channel antagonist compound of formula
3



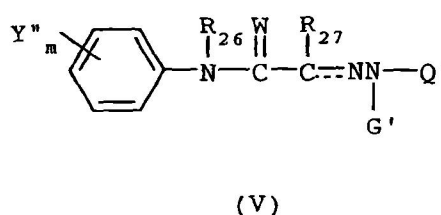
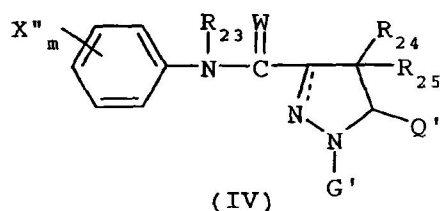
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9 wherein A is CR_4R_5 or NR_6 ;
10 W is O or S;
11 X, Y, Z, X', Y' and Z' are each independently H;
12 halogen; OH; CN; NO₂; C₁-C₆alkyl optionally
13 substituted with one or more halogen, C₁-
14 C₃alkoxy, C₁-C₃haloalkoxy, C₃-C₆cycloalkyl,
15 C₂-C₆alkenyloxy or sulfonyloxy groups;
16 C₁-C₆alkoxy optionally substituted with one or
17 more halogen, C₁-C₃alkoxy or C₃-C₆cycloalkyl

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18 groups;
 19 C_1 - C_6 alkoxycarbonyl, C_3 - C_6 cycloalkylcarbonyloxy,
 20 phenyl optionally substituted with one or
 21 more halogen, C_1 - C_4 alkyl, or C_1 - C_4 alkoxy
 22 groups;
 23 aminocarbonyloxy optionally substituted with
 24 one or more C_1 - C_3 alkyl groups;
 25 C_1 - C_6 alkoxycarbonyloxy; C_1 - C_6 alkylsulfonyloxy; C_2 -
 26 C_6 alkenyl; or $NR_{12}R_{13}$;
 27 m, p and q are each independently an integer of 1,
 28 2, 3, 4, or 5;
 29 n is an integer of 0, 1 or 2;
 30 r is an integer of 1 or 2;
 31 t is an integer of 1, 2, 3 or 4;
 32 R , R_1 , R_2 , R_3 , R_4 and R_5 are each independently H or
 33 C_1 - C_4 alkyl;
 34 R_6 is H, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxyalkyl,
 35 C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, C_2 - C_6 alkenyl, C_2 -
 36 C_6 alkynyl, C_1 - C_6 alkylcarbonyl, C_1 - C_6 alkoxy-
 37 carbonyl, C_1 - C_6 alkylthio, or C_1 - C_6 haloalkylthio;
 38 R_7 and R_8 are each independently H; halogen; C_1 -
 39 C_6 alkyl; C_1 - C_6 alkylcarbonyloxy; or phenyl
 40 optionally substituted with one or more
 41 halogen, CN, NO_2 , C_1 - C_6 alkyl, C_2 - C_6 haloalkyl,
 42 C_1 - C_6 alkoxy or C_1 - C_6 haloalkoxy groups;
 43 R_9 and R_{10} are each independently H, or C_1 - C_4 alkyl;
 44 R_{11} is H, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 -
 45 C_6 alkylcarbonyl, C_1 - C_6 alkoxycarbonyl, or C_1 -
 46 C_6 haloalkoxycarbonyl;
 47 R_{12} and R_{13} are each independently H or C_1 - C_6 alkyl;
 48 G is H; C_1 - C_6 alkyl optionally substituted with one or
 49 more halogen, C_1 - C_4 alkoxy, C_1 - C_6 haloalkoxy,
 50 CN, $NO_2S(O)_4R_{14}$, COR_{15} , CO_2R_{16} , phenyl or C_3 -
 51 C_6 cycloalkyl groups;
 52 C_1 - C_6 alkoxy; C_1 - C_6 haloalkoxy; CN; NO_2 ; $S(O)_4R_{17}$;

53 COR₁₈; CO₂R₁₉; phenyl optionally substituted
 54 with one or more halogen, CN, C₁-C₃halo-
 55 alkyl, or C₁-C₃haloalkoxy groups;
 56 C₃-C₆cycloalkyl; or phenylthio;
 57 Q is phenyl optionally substituted with one or more
 58 halogen, CN, SCN, NO₂, S(O)_uR₂₀, C₁-C₄alkyl, C₁-
 59 C₄haloalkyl, C₁-C₄alkoxyalkyl, C₁-C₆alkoxy, C₁-
 60 C₆haloalkoxy, or NR₂₁R₂₂ groups;
 61 u is an integer of 0, 1 or 2;
 62 R₁₄, R₁₅, R₁₆, R₁₈, R₁₉, R₂₁ and R₂₂ are each independently
 63 H or C₁-C₆alkyl;
 64 R₁₇ and R₂₀ are each independently C₁-C₆alkyl or
 65 C₁-C₆haloalkyl;
 66 R₃₃ is CO₂R₃₄;
 67 R₃₄ is H, C₁-C₆alkyl, C₁-C₆haloalkyl, phenyl or
 68 halophenyl; and the dotted line configuration
 69 C=N represents a double bond or a single bond; or
 70 a stereoisomer thereof.

1 17. The method according to claim 15 having a
 2 neuronal sodium channel antagonist compound of formula
 3
 4



5
 6
 7 wherein W is O or S;
 8 X' and Y' are each independently H; halogen; CN; SCN;
 9 C₁-C₆alkyl optionally substituted with one or
 10 more halogen, NO₂, CN, C₁-C₄alkoxy, C₁-
 11 C₄alkylthio, phenyl, halophenyl, C₁-
 12 C₄alkylsulfonyl, C₁-C₆haloalkylsulfonyl, or

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13 C₁-C₄alkoxycarbonyl groups;
14 C₂-C₄alkenyl; C₂-C₄haloalkenyl; C₂-C₄alkynyl; C₂-
15 C₄haloalkynyl; C₃-C₆cycloalkyl; C₃-
16 C₆halocycloalkyl; phenyl optionally substituted
17 with one or more halogen, CN, NO₂, C₁-C₄alkyl,
18 C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy,
19 C₁-C₄alkylthio, C₁-C₄alkylsulfonyl or C₁-
20 C₄haloalkylsulfonyl groups;
21 C₁-C₄alkylcarbonyl; C₁-C₄haloalkylcarbonyl; or
22 NR₂₈R₂₉;
23 m is an integer of 1, 2, 3, 4 or 5;
24 G' is phenyl optionally substituted with one or more
25 groups which may be the same or different
26 selected from X';
27 a 5-membered heteroaromatic ring containing one
28 or two heteroatoms selected from 0 or 1
29 oxygen, 0 or 1 sulfur and 0, 1 or 2
30 nitrogen atoms said 5-membered
31 heteroaromatic ring being attached via
32 carbon and being optionally substituted
33 with one or more groups which may be the
34 same or different selected from X'; or
35 a 6-membered heteroaromatic ring containing one
36 or two heteroatoms selected from 0 or 1
37 oxygen, 0 or 1 sulfur and 0, 1 or 2
38 nitrogen atoms said 6-membered
39 heteroaromatic ring being attached via
40 carbon and being optionally substituted
41 with one or more groups which may be the
42 same or different selected from X';
43 Q' is H; C₁-C₄alkyl optionally substituted with one or
44 more halogen, CN, C₁-C₃alkoxy, C₁-
45 C₄alkoxycarbonyl, or phenyl optionally
46 substituted with one or more halogen,
47 CN, NO₂, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-

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48 C₁-alkylsulfonyl or C₁-C₆alkylsulfinyl
49 groups;
50 C₂-C₆alkenyl; C₂-C₆alkynyl; or phenyl optionally
51 substituted with one to three groups,
52 which may be the same or different,
53 selected from X';
54 R₂₃, R₂₄, R₂₅, R₂₆, R₂₇, R₂₈ and R₂₉ are each
55 independently H or C₁-C₆alkyl; and the dotted
56 line configuration C=N represents a double bond or
57 a single bond; or
58 a stereoisomer thereof.⁷

59
1 18. The method according to claim 16 wherein the
2 neuronal sodium channel antagonist is a compound of
3 formula I or III.

1 19. The method according to claim 18 wherein the
2 dotted line configuration C=N represents a double bond.

1 20. The method according to claim 19 wherein the
2 formula III compound is in the S-form.

3 21. The method according to claim 20 wherein W is
4 O; X is trifluoromethoxy and is in the 4-position; Y is
5 trifluoromethyl and is in the 3-position; Z is CN and is
6 in the 4-position; A is CH₂; n is 0; m, p and q are each
7 1; R and R1 are each H; Z' is Cl; R₃₃ and G are each CO₂CH₃;
8 and Q is p-(trifluoromethoxy)phenyl.

1 22. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 cypermethrin, cyhalomethrin, cyfluthrin, permethrin,
4 ethofenprox or silafluofen.

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1 23. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 profenofos, acephate, sulprofos, malathion, diazinon,
4 methyl parathion, or terbufos.

1 24. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 methonyl, thiodicarb, or fenothiocarb.

1 25. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are amitraz,
3 chlordimeform, or chlorfenamidine.

1 26. The method according to claim 21 wherein the
2 one or more compounds selected from Group A are
3 avermectin, emamectin, milbemectin, nemadectin, or
4 moxidectin.

1 27. The method according to claim 21 wherein the
2 one or more compounds selected from Group A is
3 hydramethylnon.
4

1 28. The method according to claim 21 wherein the one
2 or more compounds selected from Group A are fipronil,
3 endosulfon, imidacloprid, acetamiprid, nitenpyram or
4 thiamethoxam.

1 29. A method for protecting a plant from infestation
2 and attack by insects which comprises applying to the
3 foliage or stem of said plant a synergistically effective
4 amount of a composition according to claim 1.

1 30. The method according to claim 29 wherein the
2 insects are *lepidoptera* or *coleoptera*.
3

33562-01L

SYNERGISTIC INSECTICIDAL COMPOSITIONS

ABSTRACT OF THE INVENTION

The present invention provides a synergistic insecticidal composition comprising as essential active ingredients a neuronal sodium channel antagonist in combination with one or more compounds selected from the group consisting of pyrethroids, pyrethroid-type compounds, organophosphates, carbamates, formamidines, macrocyclic lactonés, amidinohydrazones, GABA antagonists and acetylcholine receptor ligands.

Also provided are methods for synergistic insect control and crop protection.

33562-01L

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TRADUCCION OFICIAL No. 093

**TRADUCCION OFICIAL DE UN DOCUMENTO PRESENTADO
SIMULTANEAMENTE EN INGLES Y ESPAÑOL. TRASPASO INVENCION
"COMPOSICIONES INSECTICIDAS SINERGETICAS" A **AMERICAN CYANAMID
COMPANY.****

TRASPASO

33,562-00

(N.del T: El texto en inglés y español remite a un anexo en inglés donde aparecen las firmas de los firmantes a saber):

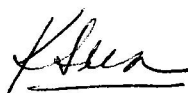
Los suscritos **Michael Frank Treacy, Raymond Frank Borysewicz, Kurt Allen Schwinghammer, Paul Erich Rensner, y Hassan Oloumi-Sadeghi**, ciudadanos de los Estados Unidos de America

De 53 Sequoia Drive, Newton, Pennsylvania 18940; 12 Albemarle Road, Hamilton Square, New Jersey 08690; 1206 University Drive, Yardley, Pennsylvania 19067; 1267 Woodthrush Court, Yardley, Pennsylvania 19067; y 1204 Goldenrod Court, Yardley, Pennsylvania 19067, respectivamente;

Firma del Inventor(es):

Firmado: Michael Frank Treacy	Fecha: Abril 28, 2000 Lugar: Princeton, NJ
Firmado: Raymond Frank Borysewicz	Fecha: Abril 25, Lugar: Princeton, NJ
Firmado: Kurt Allen Schwinghammer	Fecha: Abril 28, 2000 Lugar: Princeton, NJ
Firmado: Paul Erich Rensner	Fecha: Abril 28, 2000 Lugar: Princeton, NJ
Firmado: Hassan Oloumi-Sadeghi	Fecha: Abril 25, 2000 Princeton, NJ

Dado y firmado el abril 21, 2000
En Parsippany, New Jersey, USA


Firma CALABANCA DE AGRO
INTRODUCCION OFICIAL
No. 33-562-00

167
163

AMERICAN CYANAMID COMPANY

Por: **Egon E. Berg**
Subsecretario

Sello en altorrelieve de American Cyanamid Company


AMERICAN CYANAMID COMPANY
PRODUCTORA DE
ALCANTARA

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CERTIFICADO NOTARIAL (CORPORACION)

Firmado: **MARILYN L. MITCHELL**
Notario Público, Estado de Nueva Jersey
Mi comisión expira febrero 6, 2005

CERTIFICADO NOTARIAL (INDIVIDUAL)

Reconocimiento de la firma de **Michael Frank Treacy** en el documento en cuestión.

Firmado: **BARBARA L. LENCES**
Notario Público de Nueva Jersey
Mi comisión expira Dic. 14, 2002

CERTIFICADO NOTARIAL (INDIVIDUAL)

Reconocimiento de la firma de **Raymond Frank Borysewicz** en el documento en cuestión.

Firmado: **BARBARA L. LENCES**
Notario Público de Nueva Jersey
Mi comisión expira Dic. 14, 2002

CERTIFICADO NOTARIAL (INDIVIDUAL)

Reconocimiento de la firma de **Paul Erich Rensner** en el documento en cuestión.

Firmado: **BARBARA L. LENCES**
Notario Público de Nueva Jersey
Mi comisión expira Dic. 14, 2002


BARBARA L. LENCES
TRADUCTORA PUBLICA
ALE, COMISIONADA 2002

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165

CERTIFICADO NOTARIAL (INDIVIDUAL)

Reconocimiento de la firma de **Kurt Allen Schwinghammer** en el documento en cuestión.

Firmado: **BARBARA L. LENCES**
Notario Público de Nueva Jersey
Mi comisión expira Dic. 14, 2002

CERTIFICADO NOTARIAL (INDIVIDUAL)

Reconocimiento de la firma de **Hassan Oloumi-Sadeghi** en el documento en cuestión.

Firmado: **BARBARA L. LENCES**
Notario Público de Nueva Jersey
Mi comisión expira Dic. 14, 2002


KURT ALLEN SCHWINGHAMMER DE ASHED
TRADUCTORA OFICIAL
SES. 1000 OPTICA 1011

ESTADO DE NUEVA JERSEY
CONDADO DE MORRIS

Joan Bramhall, Secretario del Condado de Morris, en y para dicho Condado
CERTIFICA el cargo y funciones y la autenticidad de la firma y sello de

MARILYN L. MITCHELL

como Notario Público en y para dicho Condado en el momento de reconocer el
documento adjunto.

Fecha: 5-9-2000

Firmado: **Joan Bramhall**
Secretario del Condado

Firmado: **Victoria Bujont**
Secretario Delegado especial

Sello del Consulado General de Colombia en Nueva York.

ESTADO DE NUEVA JERSEY
CONDADO DE MERCER

Catherine DiCostanzo, Secretario del Condado de Mercer, en y para dicho
Condado

CERTIFICA el cargo y funciones y la autenticidad de la firma y sello de

BARBARA L. LENCES


ABRAHAM LINCOLN
TRANSLATOR OFFICIAL
BIO. MARILYN L. MITCHELL

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como Notario Público en y para dicho Condado en el momento de reconocer el documento adjunto.

Fecha: mayo 9, 2000

Firmado: **Catherine DiCostanzo**
Secretario del Condado de Mercer

Sello del Consulado General de Colombia en Nueva York.

**CERTIFICACION EN ESPAÑOL DEL CONSULADO GENERAL DE COLOMBIA
EN NUEVA YORK.**

Firmado: **José David Name C.**
Cónsul de Colombia

Sello del Consulado General de Colombia en Nueva York.

MINISTERIO DE RELACIONES EXTERIORES

CERTIFICA la firma y las funciones del funcionario consular **José Name**, bajo el número **161642**, el día mayo 16 del 2000.

Firmado: (Firma ilegible)
Jefe de Legalizaciones

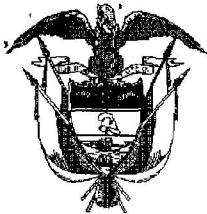
Santafé de Bogotá

[Firma]
DIRECCIÓN GENERAL DE ASUNTOS
EXTERIORES
BOGOTÁ, D.C.

JEFE DE LEGALIZACIONES
SANTAFÉ DE BOGOTÁ, D.C.

2000 MAY 18 2:35
NO SE ASUME
RESPONSABILIDAD DEL TEXTO

LA FUNDACIÓN INDICADA
DOCUMENTO RESERVA
CUYA FIRMAS APROBADA EN EL
1998
EXTERIORES
MINISTERIO DE RELACIONES EXTERIORES



CONSULADO GENERAL DE COLOMBIA

10 EAST 46TH STREET, NUEVA YORK, NY 10017
TEL. (212) 370-0004 FAX (212) 972-1725

MAY 11 2000
472
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EL SUSCRITO CONSUL DE COLOMBIA

VISTOS LOS DOCUMENTOS PRESENTADOS POR LOS INTERESADOS

C E R T I F I C A

Que el (la) Sr. **JOAN BRAMHALL**, County Clerk del ESTADO DE NEW JERSEY, verificó la firma de el (la) señor(a) **MARILYN L. MITCHELL** como notario (a) Público (a) del mismo condado, quien ejerce las funciones allí expresadas y que la firma y sello que aparecen en el documento anexo, son los que usa y acostumbra en sus actos oficiales.

Que el Notario arriba mencionada verificó la firma del señor(a) **EGON E. BERG** Quien firma el precedente documento debidamente autorizado en calidad de SECRETARIO ASISTENTE de la sociedad **AMERICAN CYANAMID COMPANY**. Sociedad organizada legalmente y existente de conformidad con las leyes del ESTADO DE MAINE, En la CIUDAD DE MADINSON .U.S.A

Que el (la) Sr. **CATHERINE DICOSTANZO**, County Clerk del ESTADO DE NEW YORK, Condado de MERCER verificó la firma de el (la) señor(a) **BARBARA L. LENCES** como notario (a) Público (a) del mismo condado, quien ejerce las funciones allí expresadas y que la firma y sello que aparecen en el documento anexo, son los que usa y acostumbra en sus actos oficiales.

Que el Notario arriba mencionada verificó la firmas del los señores **MICHAEL FRANK TREACY, RAYMOND FRANK BORYSEWICZ, PAUL ERICH RENSNER, KURT ALLEN SCHWINGHAMMER, HASSAN OLOUMI-SADEGHI**.

Que ha tenido a la vista los documentos probatorios de los hechos citados anteriormente, los cuales forman parte integral del precedente documento.

Se expide la anterior certificación de conformidad con el artículo 259 del Código de Procedimiento Civil y 480 del Código de Comercio a solicitud del interesado a los 11 días del mes de MAYO del 2000.

NO SE ASUME RESPONSABILIDAD POR EL CONTENIDO DEL DOCUMENTO ADJUNTO.

PAGADO IMPUESTO DE TIMBRE Y DERECHOS CONSULARES

VALOR CINCUENTA Y SIETE DOLARES US\$57.00 RECIBO No

23 9868/1

David Name C.
Cónsul de Colombia



MINISTERIO DE RELACIONES
EXTERIORES

1682

161642

Urme

CUYA FIRMA APARECE EN EL
DOCUMENTO DESEMPEÑA
LAS FUNCIONES INDICADAS

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2000 MAY 16 P 12:39

JEFE DE LEGALIZACIONES
SANTAFE DE BOGOTA D.C.

[Large handwritten signature]

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ASSIGNMENT CLAUSE for use in Argentina, Bolivia, Chile, Colombia, Costa Rica, Cuba, Ecuador, Guatemala, Honduras, Mexico, Nicaragua, Panama, Paraguay, Peru, El Salvador, Uruguay and Venezuela.

INSTRUCTIONS. This instrument should be used when it is desired that the letters patent be placed in the name of an Assignee. Both parties must execute this instrument and their signatures must be attested by a Notary Public. Subsequently the document must be authenticated by a Consul of the country where the application is to be filed save Argentina. Notary's attestation and Consul's certification are not required for Argentina.



COLOMBIA

33,562-00

**Power of Attorney containing
assignment clause**

(For Letters Patent of Invention)

The undersigned _____

~~SEE ATTACHED~~

hereby appoints _____

as attorneys with special and sufficient powers
to apply for and obtain from the competent
National authorities of _____

SYNERGISTIC INSECTICIDAL COMPOSITIONS

to be issued in the name of _____
AMERICAN CYANAMID COMPANY
Five Giralda Farms
Madison, New Jersey 07940
United States of America

to whom assignment has been made of all rights
and titles to the said invention for the territory
of COLOMBIA aforesaid,
without any restriction whatsoever, the considera-
tion for the said assignment being the sum of _____

Poder con Cesión

(Para Patentes de Invención)

El abajo firmado _____

~~VER ANEXO~~

nombra por el presente a _____

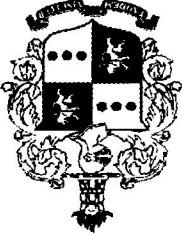
como apoderados con poder especial suficiente
para solicitar y obtener de las autoridades
nacionales _____

COMPOSICIONES INSECTICIDAS SINERGICAS

cuyo título deberá extenderse a nombre de _____
AMERICAN CYANAMID COMPANY
Five Giralda Farms
Madison, New Jersey 07940
Estados Unidos de América

a quien ha cedido todos sus derechos a la inven-
ción arriba citada en cuanto se refiere al terri-
torio de COLOMBIA

STATE OF NEW JERSEY
COUNTY OF MORRIS



I, **Joan Bramhall**, Clerk of the County of Morris holden in and for said County, do hereby certify the notary herein set forth by whom the foregoing proof, acknowledgment or affidavit taken and certified was at the time of taking such proof acknowledgment or affidavit a **NOTARY PUBLIC**, duly commissioned, sworn and residing in said County and State, and was such officer of this State, authorized to take and certify said proof, acknowledgment or affidavit as well as to take and certify proofs of acknowledgments of deeds for conveyance of lands, tenements or hereditaments and other instruments in Writing, to be recorded in said State; and full faith credit are and ought to be given to his/her official acts and I am well acquainted with the handwriting of said Notary and believe the signature to the instrument to which the certificate is attached is his/her genuine signature.

Marilyn J. Nuttall

Notary

In Testimony Whereof, I have set my hand and affixed the seal of said Court and County at Morristown.

Joan Bramhall

County Clerk

Dated: 5-9-2020

Victoria Bryant

Special Deputy Clerk

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STATE OF NEW JERSEY,
County of Mercer

ss.

I, CATHERINE DICOSTANZO, Clerk of the County of Mercer,

Do Hereby Certify that *Barbara A. Kender*

Esq., whose name is subscribed to the acknowledgment, proof or affidavit of the annexed instrument, and thereon written, is and was at the time of

taking the same, a Notary Public in and for said State, dwelling in said County, commissioned and sworn and duly authorized by the laws thereof to take the proofs and acknowledgments of deeds or other instruments of writing, and affidavits to be recorded in said State, and that I am well acquainted with the handwriting of said official, and verily believe that the signature is genuine.

Further Certify that impression of Seal of Notaries Public not required by law be filed in my office.

In Testimony Whereof, I have hereunto set my hand and affixed the seal of said County and Courts, at Trenton this *9th* ~~A.D. nineteen hundred and~~ *2000* day of

May Catherine A. Kender



Mercer County Clerk.

CERTIFICADO NOTARIAL (CORPORACION)
ESTADOS UNIDOS DE AMERICA
ESTADO DE NEW JERSEY
CONDADO DE MORRIS

Hoy 21 de Abril de 2000
compareció EGON E. BERG
conozco, quien luego de prestar juramento de solemnidad
claro y dijo:
que el es Secretario Asistente
de American Cyanamid Company

la compañía nombrada en el documento
que antecede. Una corporación organizada conforme a las
leyes del Estado de Maine, Estados Unidos de
América, domiciliada en la ciudad de Madison

Estado de New Jersey, E.U.A.
legalmente constituida para un periodo de duración que
aun no ha terminado; que el declarante está autorizado por
dicha compañía para conferir este poder y que personal-
mente ha firmado y estampado el sello de la compañía al
pie de dicho poder en nombre y representación de la com-
pañía mencionada.

El suscrito Notario ha visto los estatutos de incorpora-
ción firmados en Portland

Estado de Maine, Estados Unidos
de América con fecha Julio 23, 1907, y certifica que de con-
formidad con la legislación de dicho Estado la anterior
declaración jurada es prueba suficiente de que los hechos
sobre que ella versa son ciertos o verdaderos, de lo cual da
fe, como asimismo de que el compareciente firmo este ins-
trumento en su presencia.

MARILYN L. MITCHELL

NOTARY PUBLIC, STATE OF NEW JERSEY

Notary Public (Notario Público) My Commission Expires February 6, 2005

NOTARIAL CERTIFICATE (CORPORATION)
UNITED STATES OF AMERICA
STATE OF NEW JERSEY
COUNTY OF MORRIS

On this 21st day of April 2000
personally came EGON E. BERG
known to me, who being by me duly sworn did depose
and say that he is the Assistant Secretary
of American Cyanamid Company

The Company herein named, a Corporation
organized under the laws of the State of Maine
United States of America, domiciled in the City of Madison
State of New Jersey, U.S.A.

and legally constituted for a period of tenure not yet ex-
pired, furthermore that the deponent is authorized by said
Company to confer this Power of Attorney, and that he
personally has signed and affixed the seal of the Corpora-
tion at the foot of such power of attorney in the name and
on behalf of the Corporation mentioned.

The undersigned Notary Public has seen the Articles of
Incorporation of said Corporation executed in Portland
United States of Maine
America under date of July 23, 1907
and hereby certifies that under the laws of said State the
foregoing acknowledgement is a sufficient proof that the
facts therein contained are true, which he attests, as also
that the appearer signed this instrument in his presence.

Marilyn L. Mitchell
Marilyn L. Mitchell

CERTIFICADO NOTARIAL (INDIVIDUAL)
ESTADOS UNIDOS DE AMERICA
ESTADO DE NEW JERSEY
CONDADO DE MERCER

A los 28 días del mes de Abril
2000, compareció Michael Frank Treacy
personalmente ante mí, Notario Público en y por el conda-
do antes citado,

a quienes doy fe de conocer y me consta que es(son)
la(s) persona(s) descrita(s) y firmante(s) del documento
que precede, declarando ante mí que otorga(n) el mismo
para los fines y propósitos que en él se expresan.

Notary Public (Notario Público)

NOTARIAL CERTIFICATE (INDIVIDUAL)
UNITED STATES OF AMERICA
STATE OF NEW JERSEY
COUNTY OF MERCER

On this 28th day of April
2000 personally appeared before me, a Notary Public, in
and for the above mentioned county Michael
Frank Treacy

to me known, and known to me to be the person(s) de-
scribed herein, who executed the foregoing document, and
duly acknowledged to me that he(they) executed the same
for the uses and purposes therein expressed.

BARBARA L. LENCES
Notary Public of New Jersey
My Commission Expires Dec. 14, 2002

CERTIFICADO NOTARIAL (INDIVIDUAL)
ESTADOS UNIDOS DE AMERICA
ESTADO DE NEW JERSEY
CONDADO DE MERCER

A los 25 días del mes de Abril
2000, compareció Raymond Frank Borysewicz
personalmente ante mí, Notario Público en y por el conda-
do antes citado,

a quienes doy fe de conocer y me consta que es(son)
la(s) persona(s) descrita(s) y firmante(s) del documento
que precede, declarando ante mí que otorga(n) el mismo
para los fines y propósitos que en él se expresan.

Notary Public (Notario Público)

NOTARIAL CERTIFICATE (INDIVIDUAL)
UNITED STATES OF AMERICA
STATE OF NEW JERSEY
COUNTY OF MERCER

On this 25th day of April
2000 personally appeared before me, a Notary Public, in
and for the above mentioned county Raymond
Frank Borysewicz

to me known, and known to me to be the person(s), de-
scribed herein, who executed the foregoing document, and
duly acknowledged to me that he(they) executed the same
for the uses and purposes therein expressed.

BARBARA L. LENCES
Notary Public of New Jersey
My Commission Expires Dec. 14, 2002

CERTIFICADO NOTARIAL (INDIVIDUAL)
ESTADOS UNIDOS DE AMERICA
ESTADO DE NEW JERSEY
CONDADO DE MERCER

A los 28 días del mes de Abril
2000 compareció Paul Erich Rensner
personalmente ante mí, Notario Público en y por el conda-
do antes citado

a quienes doy fe de conocer y me consta que es(son)
la(s) persona(s) descrita(s) y firmante(s) del documento
que precede, declarando ante mí que otorga(n) el mismo
para los fines y propósitos que en él se expresan

Notary Public (Notario Público)

NOTARIAL CERTIFICATE (INDIVIDUAL)
UNITED STATES OF AMERICA
STATE OF NEW JERSEY
COUNTY OF MERCER

On this 28th day of April
2000 personally appeared before me, a Notary Public, in
and for the above mentioned county Paul Erich
Rensner

to me known, and known to me to be the person(s), de-
scribed herein, who executed the foregoing document, and
duly acknowledged to me that he(they) executed the same
for the uses and purposes therein expressed.

BARBARA L. LENCES
Notary Public of New Jersey
My Commission Expires Dec. 14, 2002

CERTIFICADO NOTARIAL (INDIVIDUAL)

ESTADOS UNIDOS DE AMERICA

ESTADO DE NEW JERSEY

CONDADO DE MERCER

as: PRINCETON

A los 25 días del mes de Abril

2000 compareció Kurt Allen Schwinghammer

personalmente ante mí, Notario Público en y por el conda-

do antes citado.

.....

.....

a quienes doy fe de conocer y me consta que es(son)

la(s) persona(s) descrita(s) y firmante(s) del documento

que precede, declarando ante mí que otorga(n) el mismo

para los fines y propósitos que en él se expresan.

Notary Public (Notario Público)

CERTIFICADO NOTARIAL (INDIVIDUAL)

ESTADOS UNIDOS DE AMERICA

ESTADO DE NEW JERSEY

CONDADO DE MERCER

as: PRINCETON

A los 25 días del mes de Abril

2000 compareció Hassan Oloumi-Sadeghi

personalmente ante mí, Notario Público en y por el conda-

do antes citado.

.....

.....

a quienes doy fe de conocer y me consta que es(son)

la(s) persona(s) descrita(s) y firmante(s) del documento

que precede, declarando ante mí que otorga(n) el mismo

para los fines y propósitos que en él se expresan.

Notary Public (Notario Público)

CERTIFICADO NOTARIAL (INDIVIDUAL)

as:

A los días del mes de

compareció

personalmente ante mí, Notario Público en y por el conda-

do antes citado

.....

.....

a quienes doy fe de conocer y me consta que es(son)

la(s) persona(s) descrita(s) y firmante(s) del documento

que precede, declarando ante mí que otorga(n) el mismo

para los fines y propósitos que en él se expresan.

Notary Public (Notario Público)

NOTARIAL CERTIFICATE (INDIVIDUAL)

UNITED STATES OF AMERICA

STATE OF NEW JERSEY

COUNTY OF MERCER

as: PRINCETON

On this 28th day of April

2000 personally appeared before me, a Notary Public, in

and for the above mentioned county Kurt

Allen Schwinghammer

.....

to me known, and known to me to be the person(s) de-

scribed herein, who executed the foregoing document, and

duly acknowledged to me that he(they) executed the same

for the uses and purposes therein expressed.

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