

CASTELLANOS & CO LTDA
ABOGADOS
Calle 94 A No. 7 A-09
Bogotá, D.C. - COLOMBIA

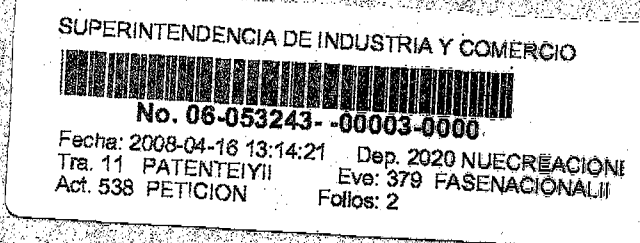
Señor

Jefe de la División de Nuevas Creaciones

Superintendencia de Industria y Comercio

Ministerio de Comercio, Desarrollo, Industria y Turismo

E. S. D.



Re.: Expediente No. 06.053.243

Solicitud del examen de patentabilidad correspondiente a la Patente PCT
Entrada en Fase Nacional, para:

**"INHIBIDORES DE CORROSION PARA FORMULACIONES PESTICIDAS
ACUOSAS"**

Solicitante: **SYNGENTA PARTICIPATIONS AG**

SOLICITUD EXAMEN DE PATENTABILIDAD **(CAPITULO II)**

Yo, **MARGARITA CASTELLANOS ABONDANO**, mayor de edad, identificada y domiciliada como aparece al pie de mi firma, obrando en mi calidad de apoderada de la sociedad solicitante, atentamente me permito solicitar a Ud. que se realice el examen de patentabilidad de la invención arriba citada, para lo cual anexo el comprobante de pago No. 08- 30.523 de Abril 15 de 2008, correspondiente a la tasa establecida para dicha solicitud.

En consecuencia, atentamente solicito a Ud. se anexe este memorial junto con el comprobante de pago al expediente correspondiente a esta solicitud de Patente PCT Entrada en Fase Nacional, y se continúe con su tramitación.

Señor Jefe,


Margarita Castellanos Abondano
C.C. No. 39.779.654 de Usaquén
T.P.A. No. 70.819 del C. S. J.
Calle 94 A No. 7 A-09 - Bogotá, D.C.
Teléfono (PBX): 610 7420

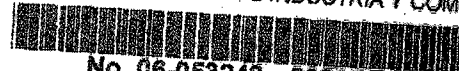
16 ABR. 2008

Bogotá,
MCA/gcb/P1361 (6052-FNPCT)

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-053243- -00003-0000

Fecha: 2008-04-16 13:14:21 Dep. 2020 NUECREACION
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RECIBO OFICIAL DE CAJA : 06 - 30,523
FECHA : ABRIL 15 DE 2008

===== CONSIGNACION =====

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	NO. PAGO	FECHA PGO	VR. PAGO
ALVARO CASTELLANOS	CONSIGNACION	BANCO DE BOGOTA	062754387	316175	15/04/2008	4,910,000.00

===== CONCEPTO =====

CANT.	CONCEPTO	TOTAL CONCEPTO
1	50003-01-01 SOLICITUDES	
	114 PTC CAP-11 EXAMEN DE PATENTIBILIDAD	210,000.00
	TOTAL :	210,000.00

MON: DOSCIENTOS DIEZ MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 06-53243

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **581** DE

FECHA **31 DE OCTUBRE DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA

LEY EXPIRA EL **31 DE ENERO DE 2008**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X



US005416061A

United States Patent [19]

Hewett et al.

[11] Patent Number: **5,416,061**[45] Date of Patent: **May 16, 1995**[54] **HERBICIDAL COMBINATIONS OF
BROMOXYNIL WITH SELECTED
2-BENZOYLCYCLOHEXANE-1,3-DIONES**[75] Inventors: **Richard H. Hewett; Brian M.
Luscombe, both of Ongar, England**[73] Assignee: **Rhone-Poulenc Agriculture Ltd,
Essex, England**[21] Appl. No.: **163,830**[22] Filed: **Dec. 9, 1993****Related U.S. Application Data**

[63] Continuation of Ser. No. 867,522, Apr. 13, 1992, abandoned.

Foreign Application Priority Data

Apr. 17, 1991 [GB] United Kingdom 9108199

[51] Int. Cl.⁶ A01N 37/34; A01N 35/06[52] U.S. Cl. 504/141; 504/118;
504/310; 504/348

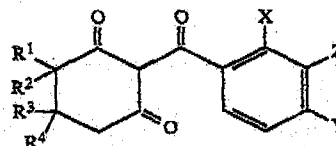
[58] Field of Search 504/141, 118, 310, 348

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(List continued on next page.)*Primary Examiner*—Richard L. Raymond*Assistant Examiner*—B. Bembenick*Attorney, Agent, or Firm*—Burns, Doane, Swecker &
Mathis**[57] ABSTRACT**Herbicidal compositions comprising (a) bromoxynil and
(b) a 2-benzoylcyclohexane-1,3-dione derivative of general formula I:

wherein

(i) Z represents the hydrogen atom;

R¹ and R² which may be the same or different each represents the hydrogen atom or the methyl group.R³ and R⁴, which may be the same or different each represents the hydrogen atom or the methyl group.

X represents the chlorine atom or the nitro group,

Y represents the methylsulphonyl or trifluoromethyl group; or

(ii) Z represents the chlorine atom;

R¹, R², R³ and R⁴ each represent the hydrogen atom,

X represents the chlorine atom; and

Y represents the methylsulphonyl group; salts thereof with agriculturally acceptable bases and their use in controlling weeds is described.

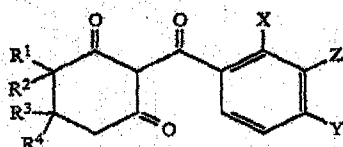
43 Claims, 12 Drawing Sheets

HERBICIDAL COMBINATIONS OF BROMOXYNIL WITH SELECTED 2-BENZOYLCYCLOHEXANE-1,3-DIONES

This application is a continuation of application Ser. No. 07/867,522, filed Apr. 13, 1992, abandoned.

The present invention relates to a method of controlling the growth of weeds by the application of bromoxynil or an agriculturally acceptable salt or ester thereof and certain 2-benzoylcyclohexane-1,3-diones or agriculturally acceptable salts thereof, and to compositions containing them.

The 2-benzoylcyclohexane-1,3-dione derivatives used in the present invention are of general formula I:



wherein

(i) Z represents the hydrogen atom;

R¹ and R² which may be the same or different, each represents the hydrogen atom or the methyl group,

R³ and R⁴ which may be the same or different, each represents the hydrogen atom or the methyl group,

X represents the chlorine atom or the nitro group, Y represents the methylsulphonyl or trifluoromethyl group; or

(ii) Z represents the chlorine atom;

R¹, R², R³ and R⁴ each represent the hydrogen atom,

X represents the chlorine atom; and

Y represents the methylsulphonyl group; and salts thereof with agriculturally acceptable bases [which are embraced by the general formulae in the specifications of European Patent Publications No. 135191, 137963 and 186118 describing pre- and/or post emergence herbicides].

In certain cases the groups R¹, R², R³ and R⁴ contribute to optical and/or stereoisomerism. All such forms are embraced by the present invention.

The compounds of general formula I include

A. 2-(2-chloro-4-methylsulphonylbenzoyl)cyclohexane-1,3-dione

B. 2-(2-chloro-4-methylsulphonylbenzoyl)-5,5-dimethylcyclohexane-1,3-dione

C. 2-(2-chloro-4-methylsulphonylbenzoyl)-4,4-dimethylcyclohexane-1,3-dione

D. 2-(4-methylsulphonyl-2-nitrobenzoyl)cyclohexane-1,3-dione

E. 2-(2-nitro-4-trifluoromethylbenzoyl)cyclohexane-1,3-dione

F. 2-(2-chloro-4-trifluoromethylbenzoyl)cyclohexane-1,3-dione

G. 2-(4-methylsulphonyl-2-nitrobenzoyl)-5,5-dimethylcyclohexane-1,3-dione

H. 2-(2-nitro-4-trifluoromethylbenzoyl)-5,5-dimethylcyclohexane-1,3-dione

I. 2-(2-nitro-4-trifluoromethylbenzoyl)-4,4-dimethylcyclohexane-1,3-dione

J. 2-(4-methylsulphonyl-2-nitrobenzoyl)-4,4-dimethylcyclohexane-1,3-dione

K. 2-(2-nitro-4-trifluoromethylbenzoyl)-5-methylcyclohexane-1,3-dione

L. 2-(2-chloro-4-methylsulphonylbenzoyl)-5-methylcyclohexane-1,3-dione

M. 2-(2-nitro-4-methylsulphonylbenzoyl)-5-methylcyclohexane-1,3-dione

N. 2-(2,3-dichloro-4-methylsulphonylbenzoyl)cyclohexane-1,3-dione

The letters are assigned to the above compounds for identification and reference hereinafter.

Bromoxynil [3,5-dibromo-4-hydroxybenzonitrile] may be used for post-emergence weed control in maize, wheat and barley. Although giving control of a wide range of broad-leaf weeds, control of some important species for example *Amaranthus retroflexus*, *Ipomoea purpurea* and *Sida spinosa* is unreliable. Owing to a lack of residual activity in the soil bromoxynil does not control the weeds which emerge after application. Bromoxynil has no useful activity against grass or sedge weeds.

It is to be understood that where in this specification reference is made to "bromoxynil" it is intended to refer, where the context so permits, to bromoxynil [3,5-dibromo-4-hydroxybenzonitrile] in the form of the parent phenol (acid equivalent: a.e.), or an agriculturally acceptable salt or ester thereof, preferably a metal or amine salt or an ester thereof with an alkanolic acid conjoining from 2 to 10 carbon atoms.

As a result of research and experimentation it has now been discovered that the use of 2-benzoylcyclohexane-1,3-dione derivatives in combination with bromoxynil add to its capabilities of controlling a wide spectrum of broad-leaf weeds, grasses and sedges by both foliar activity and residual soil activity.

In addition to this it has been found that the combined herbicidal activity of combinations of 2-benzoylcyclohexane-1,3-dione derivatives with bromoxynil against certain species is greater than expected when applied post-emergence (e.g. as a post-emergence spray) i.e. the herbicidal activity of combinations of 2-benzoylcyclohexane-1,3-dione derivatives with bromoxynil showed an unexpected degree of synergism (as defined either by P. M. L. Tamme, Netherlands Journal of Plant Pathology, 70 (1964), pp 73-80 in a paper entitled "Isoboles, a graphic representation of synergism in pesticides", and by L. E. Limpel et al., Proceedings of the North East Weed Control Conference, 16 (1962), pp 48-53 in a paper entitled "Weed Control by dimethyl tetrachloro terephthalate alone and in certain mixtures").

The remarkable synergistic effect gives improved reliability of control of a number of weed species and allows for a reduction in the amount of active ingredients employed.

Accordingly the present invention provides a method for the control of the growth of weeds at a locus which comprises applying to the locus (a) bromoxynil and (b) a 2-benzoylcyclohexane-1,3-dione derivative of general formula I as hereinbefore defined or a salt thereof with an agriculturally acceptable base. For this purpose, the 2-benzoylcyclohexane-1,3-dione herbicide and bromoxynil are normally used in the form of herbicidal compositions (i.e. in association with compatible diluents or carriers and/or surface-active agents suitable for use in herbicidal compositions), for example as hereinafter described.

Preferred compounds of general formula I are those wherein

Z represents the hydrogen atom; and

R³ and R⁴ both represent hydrogen atoms or both represent methyl groups.

Further preferred compounds of general formula I are those wherein R¹ and R² both represent hydrogen atoms or both represent methyl groups, and R³ and R⁴ both represent hydrogen atoms or both represent methyl groups.

The amounts of the 2-benzoyl-cyclohexane-1,3-dione herbicide and bromoxynil applied vary with the nature of the weeds, the compositions used, the time of application, the climatic and edaphic conditions and (when used to control the growth of weeds in crop-growing areas) the nature of the crops. When applied to a crop-growing area, the rate of application should be sufficient to control the growth of weeds without causing substantial permanent damage to the crop. In general, taking these factors into account, application rates from 0.5 g to 500 g a.e. of the 2-benzoyl-cyclohexane-1,3-dione herbicide and from 2 g to 350 g a.e. of bromoxynil per hectare give good results. However, it is to be understood that higher or lower applications rates may be used, depending upon the particular problem of weed control encountered.

The cyclohexane herbicide and bromoxynil in combination may be used to control selectively the growth of weeds, for example to control the growth of those species hereinafter mentioned, by pre- or, preferably, post-emergence application in a directional or non-directional fashion e.g. by directional or non-directional spraying, to a locus of weed infestation which is an area used, or to be used, for growing crops, for example cereals, e.g. wheat, barley, oats, rye, maize and rice, soya beans, field and dwarf beans, peas, lucerne, cotton, peanuts, flax, onions, carrots, oilseed rape, sunflower, and permanent or sown grassland before or after sowing of the crop or before or after emergence of the crop. For the selective control of weeds at a locus of weed infestation which is an area used, or to be used, for the growing of crops, e.g. the crops hereinbefore mentioned, application rates from 25 g to 500 g a.e. of the 2-benzoylcyclohexane-1,3-dione herbicide and from 150 g to 350 g a.e. of bromoxynil per hectare are particularly suitable.

According to a feature of the present invention, there is provided a method for the control of the growth of weeds at a maize, wheat or barley crop locus which comprises applying to the locus (a) bromoxynil and (b) a 2-benzoylcyclohexane-1,3-dione derivative of general formula I as hereinbefore defined or a salt thereof with an agriculturally acceptable base. Preferably the application rates of (a) and (b) are from 2 to 350 preferably from 150 to 350 (more preferably from 200 to 300)g a.e./ha and from 0.5 to 500 and preferably from 25 to 500 more preferably 50 to 400 (for example 50 to 250)g acid equivalent/ha respectively in proportions of 700:1 to 1:250, preferably 14:1 to 1:3.33, more preferably 6:1 to 1:2 and more preferably 6:1 to 1:1.25 wt/wt of acid equivalent (a) to acid equivalent (b).

This method may be used to control a broad spectrum of weed species in maize, wheat and barley crops by post-emergence application without significant permanent damage to the crop. The combined use described above provides both foliar and residual activity.

By the term 'pre-emergence application' is meant application to the soil in which the weed seeds or seedlings are present before emergence of the weeds above the surface of the soil. By the term 'post-emergence application' is meant application to the aerial or exposed

portions of the weeds which have emerged above the surface of the soil. By the term 'foliar activity' is meant herbicidal activity produced by application to the aerial or exposed portions of the weeds which have emerged above the surface of the soil. By the term 'residual activity' is meant herbicidal activity produced by application to the soil in which weed seeds or seedlings are present before emergence of the weeds above the surface of the soil, whereby seedlings present at the time of application or which germinate subsequent to application from seeds present in the soil are controlled.

Weeds that may be controlled by the method include: from broad-leaf weeds, *Abutilon theophrasti*, *Amaranthus retroflexus*, *Ambrosia trifida*, *Amsinckia intermedia*, *Anthemis arvensis*, *Bidens pilosa*, *Brassica kaber*, *Chenopodium album*, *Ipomoea* spp. (e.g. *I. hederacea*, *I. purpurea*), *Kochia scoparia*, *Matricaria* spp. *Polygonum* spp. (e.g. *P. aviculare*, *P. convolvulus*, *P. pennsylvanicum*, *P. Persicaria*, *P. scabrum*), *Raphanus raphanistrum*, *Sesbania exaltata*, *Sida spinosa*, *Solanum* spp. (e.g. *S. elaeagnifolium*, *S. nigrum*, *S. nostratum*, *S. sarachoides*), *Sonchus oleraceus*, *Stellaria media*, *Thlaspi arvense*, *Xanthium pennsylvanicum*, and from grass weeds, *Digitaria sanguinalis*, *Echinochloa crus-galli* and *Eleusine indica*, and from sedges, *Cyperus* spp. (e.g. *C. esculentus* and *C. rotundus*).

In accordance with usual practice, a tank mix may be prepared prior to use by combining separate formulations of the individual herbicidal components, or separate formulations may be applied in a time-separated manner.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an ED50 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound A with bromoxynil applied to *Abutilon theophrasti* seedlings;

FIG. 2 is an ED90 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound A with bromoxynil applied to *Amaranthus retroflexus* seedlings;

FIG. 3 is an ED90 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound A with bromoxynil applied to *Brassica kaber* seedlings;

FIG. 4 is an ED90 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound D with bromoxynil applied to *Ipomoea* species seedlings;

FIG. 5 is an ED50 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound D with bromoxynil applied to *Echinochloa crus-galli* seedlings;

FIG. 6 is an ED50 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound E with bromoxynil applied to *Ipomoea* species seedlings;

FIG. 7 is an ED50 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound E with bromoxynil applied to *Sida spinosa* seedlings;

FIG. 8 is an ED90 isobole plot calculated from observed values (□) and a corresponding plot of expected additive values (—) for mixtures of Compound E

by weight of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative(s).

The herbicidal compositions may contain both a diluent or carrier and a surface-active (e.g. wetting, dispersing, or emulsifying) agent. Surface-active agents which may be present in herbicidal compositions of the present invention may be of the ionic or non-ionic types, for example sulphoricinoleates, products based on condensates of ethylene oxide with nonyl- or octyl-phenols, or carboxylic acid esters of anhydrosorbitols which have been rendered soluble by etherification of the free hydroxy groups by condensation with ethylene oxide, alkali and alkaline earth metal salts or sulphuric acid esters and sulphonic acids such as dinonyl- and dioctyl-sodium sulphonosuccinates and alkali and alkaline earth metal salts of high molecular weight sulphonic acid derivatives such as sodium and calcium lignosulphonates. Examples of suitable solid diluents or carriers are aluminium silicate, talc, calcined magnesia, kieselguhr, tricalcium phosphate, powdered cork, absorbent carbon black and clays such as kaolin and bentonite. The solid compositions (which may take the form of dusts, granules or wettable powders) are preferably prepared by grinding bromoxynil and the 2-benzoylcyclohexane-1,3-dione derivative with solid diluents or by impregnating the solid diluents or carriers with solutions of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative in volatile solvents, evaporating the solvents and, if necessary, grinding the products so as to obtain powders. Granular formulations may be prepared by absorbing bromoxynil and the 2-benzoylcyclohexane-1,3-dione derivative (dissolved in volatile solvents) onto the solid diluents or carriers in granular form and evaporating the solvents, or by granulating compositions in powder form obtained as described above. Solid herbicidal compositions, particularly wettable powders, may contain wetting or dispersing agents (for example of the types described above), which may also, when solid, serve as diluents or carriers.

Liquid compositions according to the invention may take the form of aqueous, organic or aqueous-organic solutions, suspensions and emulsions which may incorporate a surface-active agent. Suitable liquid diluents for incorporation in the liquid compositions include water, acetophenone, cyclohexanone, isophorone, toluene, xylene and mineral, animal and vegetable oils (and mixtures of these diluents). Surface-active agents, which may be present in the liquid compositions, may be ionic or non-ionic (for example of the types described above) and may, when liquid, also serve as diluents or carriers.

Wettable powders and liquid compositions in the form of concentrates may be diluted with water or other suitable diluents, for example mineral or vegetable oils, particularly in the case of liquid concentrates in which the diluent or carrier is an oil, to give compositions ready for use. When desired, liquid compositions of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative may be used in the form of self-emulsifying concentrates containing the active substances dissolved in the emulsifying agents or in solvents containing emulsifying agents compatible with the active substances, the simple addition of water to such concentrates producing compositions ready for use.

Liquid concentrates in which the diluent or carrier is an oil may be used without further dilution using the electrostatic spray technique.

Herbicidal compositions according to the present invention may also contain, if desired, conventional adjuvants such as adhesives, protective colloids, thickeners, penetrating agents, stabilisers, sequestering agents, anti-caking agents, colouring agents and corrosion inhibitors. These adjuvants may also serve as carriers or diluents.

Preferred herbicidal compositions according to the present invention are aqueous suspension concentrates which comprise from 10 to 70% w/v of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative, from 2 to 10% w/v of surface-active agent, from 0.1 to 5% w/v of thickener and from 15 to 87.9% by volume of water; wettable powders which comprise from 10 to 90% w/w of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative, from 2 to 10% w/w of surface-active agent and from 8 to 88% w/w of solid diluent or carrier; liquid water soluble concentrates which comprise from 10 to 30% w/v of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative, from 5 to 25% w/v of surface-active agent and from 45 to 85% by volume of water-miscible solvent, e.g. dimethylformamide; liquid emulsifiable suspension concentrates which comprise from 10 to 70% w/v of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative, from 5 to 15% w/v of surface-active agent, from 0.1 to 5% w/v of thickener and from 10 to 84.9% by volume of organic solvent; granules which comprise from 2 to 10% w/w of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative, from 0.5 to 2% w/w of surface-active agent and from 88 to 97.5% w/w of granular carrier; and emulsifiable concentrates which comprise from 0.05 to 90% w/v, and preferably from 1 to 60% w/v, of bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative, from 0.01 to 10% w/v, and preferably from 1 to 10% w/v, of surface-active agent and from 9.99 to 99.94%, and preferably from 39 to 98.99%, by volume of organic solvent.

Herbicidal compositions according to the present invention may also comprise bromoxynil and 2-benzoylcyclohexane-1,3-dione derivative in association with, and preferably homogeneously dispersed in, one or more other pesticidally active compounds and, if desired, one or more compatible pesticidally acceptable diluents or carriers, surface-active agents and conventional adjuvants as hereinbefore described. Examples of other pesticidally active compounds which may be included in, or used in conjunction with, the herbicidal compositions of the present invention include herbicides, for example to increase the range of weed species controlled, for example, alachlor (2-chloro-2,6-diethyl-N-methoxymethylacetanilide), bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide), cyanazine (2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-1,3,5-triazine), 2,4-D ((2,4-dichlorophenoxy)acetic acid), MCPA [4-chloro-2-methylphenoxyacetic acid], sulphonyl ureas e.g. nicosulfuron [2-(4',6'-dimethoxypyrimidin-2'-ylcarbamoylsulfamoyl)-N,N-dimethylnicotinamide] and CMPP (also known as mecoprop) [(±)-2-(4-chloro-2-methylphenoxy)propionic acid]; insecticides for example carbamates (e.g. carbofuran), organo-phosphates (e.g. chlorpyrifos), synthetic pyrethroids (e.g. cypermethrin), acyl ureas (e.g. teflubenzuron) and *Bacillus thuringiensis*; and fungicides for example metalaxyl, carboxin and captan. Other biologically active materials which may be included in, or used in conjunction with, the herbicidal compositions of the present invention are plant growth regulators and fertilizers containing, for example, nitrogen,

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23F 11/08, C09K 5/00	A1	(11) International Publication Number: WO 99/07918 (43) International Publication Date: 18 February 1999 (18.02.99)
(21) International Application Number: PCT/US98/15656 (22) International Filing Date: 29 July 1998 (29.07.98) (30) Priority Data: 08/908,040 11 August 1997 (11.08.97) US (71) Applicant: PRESTONE PRODUCTS CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06810-5109 (US). (72) Inventors: FROST, Richard, A.; Whaley Lake Road, R.R. 2, Box 321, Holmes, NY 12531 (US). GERSHUN, Aleksei, V.; 80 Lancaster Street, Oakville, CT 06779 (US). MERCER, William, C.; 42 Candlewood Shores Road, Brookfield, CT 06804 (US). WOYCIESJES, Peter, M.; 37 Westwood Road, Woodbury, CT 06798 (US). (74) Agents: GROSS, Marta, E. et al.; Fish & Neave, 1251 Avenue of the Americas, New York, NY 10020 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: METHOD OF INHIBITING CORROSION OF FLUX-TREATED METAL SURFACES (57) Abstract This invention relates to a method of inhibiting the corrosion of flux-treated metal surfaces. The method comprises the step of contacting the flux-treated metal surface with a formulation comprising a corrosion inhibitor composition comprising one or more mono-carboxylic acids, or salts or isomers thereof, and an effective amount of a corrosion inhibiting surface active agent such as a water soluble alkali or alkaline earth metal nitrate salt. This method has been demonstrated to be a surprisingly effective means to inhibit corrosion of flux-treated metal surfaces found in the cooling systems of internal combustion engines.		

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METHOD OF INHIBITING CORROSION OF FLUX-TREATED METAL SURFACES

Field of the Invention

The present invention relates generally to a method of inhibiting corrosion of flux-treated metal surfaces. More particularly, the present invention relates to the use of an organic acid corrosion inhibitor composition comprising a surface active agent to provide prolonged protection to flux-treated metal surfaces typically found in industrial and commercial heat exchangers, such as those in internal combustion engines.

Background of the Invention

Corrosion has long been a problem when certain metals or alloys are used in applications in which they come into contact with an aqueous medium. For example, in heat-transfer systems, such as those found in internal combustion engines, alcohol-based heat transfer fluids (i.e., antifreezes) can be very corrosive to the metal surfaces of the heat-transfer systems. Compounding this problem is that the corrosion is accelerated under normal engine operating conditions (i.e., high temperatures and pressures). Corrosion inhibitors have been used to address these problems by protecting the metal surfaces in industrial and commercial heating and/or cooling systems such as heat exchangers used in the automotive industry (e.g., radiators which control engine operating temperatures, condensers and evaporators in air conditioning systems, and heater cores which provide heat to passenger compartments).

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Heat exchangers for cars and light trucks have traditionally been constructed of soldered brass. More recently, however, in order to meet new environmental standards mandating improved fuel economy and reduced emissions, automotive manufacturers have begun using more lightweight metals (e.g., aluminum). See, e.g., Ward's Auto World, p.22 (Sept., 1996); Ward's 1996 Automotive Yearbook, p.27 (58th ed. 1996). Accordingly, heat exchangers in cars and light duty trucks are now being constructed using aluminum components. Typical aluminum components in heat exchangers include the tubes through which the coolant passes and in which the heat exchange occurs, the fins that are between the tubes to transfer heat from the tubes to the outside air, the header plates that hold the tubes and fins in place, and, in the case of heater cores, the end tanks that transfer the fluid between the tubes and the engine. See, e.g., Fortin et al., "Aluminum Materials and Processes for Aluminum Heat Exchanger Applications," SAE Technical Paper No. 852228 (1985). However, aluminum surfaces are particularly susceptible to corrosion. See, Darden et al., "Monobasic/Diacid Combination as Corrosion Inhibitors in Antifreeze Formulations," Worldwide Trends in Engine Coolants, Cooling System Materials and Testing, SAE Int'l SP-811, Paper #900804, pp. 135-51 (1990) ("SAE SP-811").

During the assembly of automotive heat exchangers, the aluminum components are typically joined together by a brazing process which generally involves joining these aluminum-containing components with a brazing alloy (i.e., an aluminum alloy with a melting point substantially lower than that of the components to be joined). The aluminum components to be joined are "brazed" by holding them together in a jig with the brazing alloy adjacent to or between these components, then heating them in a furnace to a temperature that will melt the brazing alloy without melting the components. The brazing process is described in "Base Metals, Brazing Filler Metals and Fluxes," Aluminum Brazing Handbook, p. 24 (Jan. 1990).

One of the problems with brazing aluminum is that aluminum is prone to oxidation. Aluminum oxidation is promoted by high temperatures and the presence of oxygen and water vapor and can reduce the strength and durability of a brazed joint. One brazing method which avoids this problem is the controlled atmosphere brazing

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("CAB") process. The CAB process generally involves pre-assembly of the aluminum components in a jig, spraying of the pre-assembled components with a flux, and then followed by introduction into an inert and controlled atmosphere brazing oven. The CAB process is the preferred brazing method, as compared to other brazing methods that also avoid aluminum oxide formation (e.g., vacuum brazing), because it is cost effective and generally produces higher quality heat exchangers with reduced scrap rates. The CAB process is described in United States Patent Nos. 5,422,191; 5,360,158; 5,333,777; 3,971,501 and 3,951,328; Cooke et al., "Furnace Brazing of Aluminum with a Non-Corrosive Flux," SAE Technical Paper No. 780300 (1978); Claydon et al., "Brazing Aluminum Automotive Heat Exchanger Assemblies Using a Non-Corrosive Flux Process," SAE Technical Paper No. 830021 (1983); D. L. Childree, "A New Al-Si-Li Filler Metal that Enhances Brazeability of High-Strength Alloys in CAB and Vacuum," SAE Int'l SP-1175, Technical Paper No. 9602447 (1996); Brazing Handbook, American Welding Society (1991).

In the CAB process, the flux, which typically consists of alkali metal or alkaline earth metal fluorides or chlorides, serves a number of important functions. These include removing the aluminum oxide coating present on the exposed metal and brazing alloy surfaces, preventing reformation of the aluminum oxide layer during brazing, and enhancing the flow of the brazing alloy.

It has been found that the use of this flux in heat exchangers assembled by the CAB process results in residual flux on the surfaces of the aluminum components. The aluminum surfaces that generally are exposed to the flux residue include the inside of the heat exchanger tubes, i.e., radiator and/or heater core. However, because the commonly-used fluoride-based fluxes are considered non-corrosive to aluminum, the presence of residual flux per se has not been considered a problem.

Aluminum heat exchangers manufactured by the CAB process, and thus containing flux-treated aluminum surfaces, are fairly common in automotive and light truck applications and are currently in use by at least one major heat exchanger manufacturer. Ando et al., "Development of Aluminum Radiators Using the Nocolok

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Brazing Process -- Corrosion Resistance of New Aluminum Radiators by Applying a Nocolok Brazing Process," SAE Technical Paper No. 870180 (1987); Park et al., "New Vacuum Brazed Aluminum Radiators for Ford Light Trucks," SAE Technical Paper No. 860078 (1986). There have been no reported problems associated with corrosion of these heat exchangers when used with antifreeze formulations containing conventional corrosion inhibitors such as triazoles, thiazoles, borates, silicates, phosphates, benzoates, nitrates, nitrites and molybdates. However, such conventional corrosion inhibitors may have problems in some applications, including expense and inadequate long-term protection. See United States patent No. 4,946,616, col. 1, lines 31-45; United States patent No. 4,588,513, col. 1, lines 55-64; SAE SP-811, pp. 137-38. Accordingly, automobile manufacturers have begun using, and several now require, organic acid based (or extended life) corrosion inhibitors. A number of organic acid corrosion inhibitors have been described. See, e.g., United States patent Nos. 4,382,008, 4,448,702 and 4,946,616; see also, United States patent application Serial No. 08/567,639, incorporated herein by reference.

However, several formulations comprising mono-carboxylic acid(s), even those previously demonstrated to be effective aluminum corrosion inhibitors, have been unable to adequately protect CAB manufactured (i.e., flux-treated) aluminum surfaces. Further, while several aluminum corrosion inhibitors are known, many of these corrosion inhibitors are undesirable or unacceptable for the organic acid based antifreeze formulations used today. For example, phosphate salts, known to inhibit aluminum corrosion, are unacceptable because they have been prohibited for use in organic acid formulations by a number of original equipment automotive manufacturers. See, e.g., General Motors Engineering Standards, "Long-Life Automotive Engine Coolant Antifreeze Concentrate - Ethylene Glycol," Specification No. GM 6277M; Ford Engineering Material Specifications, "Coolant, Organic Additive Technology, Concentrate," Specification No. WSS-M97B44-C; Chrysler Corporation Engineering Standards, "Engine Coolant - Glycol Type - Inhibited - Production and Service Use," Standard No. MS-9769. Similarly, sodium silicate, also a known aluminum corrosion inhibitor, is prohibited by General Motors and Ford.

Moreover, sodium nitrate, known to effectively prevent aluminum pitting corrosion in conventional coolant formulations, has been reported to be much less effective in preventing pitting-corrosion than organic acid based inhibitors. See United States Patent No. 4,647,392, col. 12.

5 Accordingly, there remains a need for a method using mono-carboxylic acid-based corrosion inhibitors to protect flux-treated metal surfaces, especially those found in automotive heat exchangers.

Summary of the Invention

10 The present invention provides a method of inhibiting the corrosion of flux-treated metal surfaces. The inventive method comprises the step of contacting the flux-treated metal surface with a formulation comprising a corrosion inhibitor composition comprising one or more mono-carboxylic acids, or salts or isomers thereof, and a corrosion inhibiting surface active agent.

15 The mono-carboxylic acid used in the corrosion inhibitor composition may be selected from the group consisting of saturated and unsaturated aliphatic, and aromatic, mono-carboxylic acids, and inorganic and organic salts and isomers thereof, and any combination thereof. The corrosion-inhibiting surface active agent may be any organic or inorganic nitrate salt including water soluble alkali or alkaline earth metal
20 nitrate salts ←

 The method of this invention has been demonstrated to be a surprisingly effective means to inhibit corrosion of flux-treated metal surfaces found in the cooling systems of internal combustion engines. For this application, the aqueous medium used is an antifreeze coolant formulation comprising a liquid alcohol freezing point
25 depressant, from about 0.1% to about 5.5% by weight of the corrosion inhibitor composition, and from about 10% to about 90% by weight water.

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Detailed Description of the Invention

In order that the invention herein described may be more fully understood, the following detailed description is set forth.

The present invention provides an effective low cost method for
5 inhibiting corrosion of flux-treated metal surfaces (e.g., aluminum or aluminum alloys used in the CAB process) that are in contact with aqueous systems. The inventive method comprises the step of contacting the flux-treated metal surface with a formulation comprising a corrosion inhibitor composition comprising one or more
10 mono-carboxylic acids, or salts or isomers thereof, and an effective amount of a corrosion inhibiting surface active agent.

The corrosion-inhibiting surface active agent may be any organic or inorganic nitrate salt including water soluble alkali or alkaline earth metal nitrate salts. Examples of such nitrate salts include sodium, potassium, calcium, magnesium and lithium salts. Ammonium and amine salts of these compounds may also be used. The
15 preferred surface active agents are alkali metal nitrate salts, and more preferred is sodium nitrate (i.e., NaNO_3). ←

The mono-carboxylic acid used in the corrosion inhibitor composition may be selected from the group consisting of saturated and unsaturated aliphatic, and aromatic, mono-carboxylic acids, and inorganic and organic salts and isomers thereof,
20 and combinations thereof. Preferred mono-carboxylic acids include C_4 - C_{12} mono-carboxylic acids, or inorganic or organic salts or isomers thereof, or combinations thereof. The more preferred mono-carboxylic acids include mixtures having a major amount of a C_8 mono-carboxylic acid component (e.g., neo-octanoic acid and/or 2-ethyl hexanoic acid, more preferably 2-ethyl hexanoic acid) and neo-
25 decanoic acid. Where the mixture of a C_8 mono-carboxylic acid component and neo-decanoic acid is used, the preferred mixture comprises the C_8 mono-carboxylic acid component and neo-decanoic acid in the weight ratio of about 3:1. See United States patent application Serial No. 08/567,639.

The present method may be used in a number of corrosion-inhibiting
30 applications, including, but not limited to, antifreeze formulations used in the cooling

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES

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ASUNTO	Radicación	06053243
	Trámite	011
	Evento	379
	Actuación	519
	Oficio	<u>1 4768</u>
	Folios	15

Patente de Invención ☒ Patente de Modelo de Utilidad ☐

Vía Nacional ☐

Vía PCT (fase nacional) ☒ Cap. I ☐ Cap. II ☒

No. Sol. Internacional: PCT/US2004/038945
Fecha de Presentación Internacional: 2004-11-19

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

Capítulo descriptivo: Folios 25 a 39 y 42 tal y como fueron presentados.
Capítulo reivindicatorio: Folios 40 a 41 tal y como fueron presentados.
Prioridad: Folio 1 US 60/527555 2003-12-05

2. Objeto de la invención

Título de la solicitud: Inhibidores de corrosión para formulaciones pesticidas acuosas. Folio 1.

Objeto de la invención: El objeto de la presente solicitud de patente de invención se refiere concentrados pesticidas que comprenden al menos un pesticida y una sal de nitrato iónica.

Según la descripción el problema técnico planteado en la presente solicitud de patente radica en que la presencia de sales disueltas como cloruros iónicos o ingredientes activos pesticidas de carácter ácido, en forma de sal o complejo metálico, aceleran la corrosión de las superficies metálicas. Para solucionar este problema técnico la solicitud plantea composiciones pesticidas acuosas que contiene una sal de nitrato la cual reduce significativamente la corrosión de superficies metálicas, incluso con niveles de pH ácidos y presencia de sal.

El objeto de la solicitud definido anteriormente se clasificó en la IPC A01N 25/02 A01P3/00; 5/00; 7/02; 7/04; 13/00.

3. De la solicitud de Patente

El título de la invención debe ser modificado, y definir específicamente el objeto de la invención.

3.1. Reivindicaciones (artículo 30 D 486)

El capítulo reivindicatorio es presentado en un lenguaje muy amplio y no define específicamente el alcance de la invención. Así por ejemplo expresiones como "al menos, una cantidad, optativamente, inferior ó igual, o inferior" son muy amplias y no definen el objeto de la invención.

En consecuencia el capítulo reivindicatorio resulta ser una generalización sin sustento en la descripción. Nótese que en el capítulo descriptivo se divulga un único ingrediente activo para el cual se demuestra un efecto. No obstante dicho ejemplo es insuficiente para respaldar la amplia generalización presentada en el capítulo reivindicatorio "5-90% en peso de al menos un pesticida". El solicitante debe limitar el alcance de su invención.

Por último sírvase suprimir la frase "...efectiva para reducir la corrosión de superficies metálicas" puesto que es explicativa, hace referencia al problema técnico, es decir caracteriza la composición por el objetivo a alcanzar y no define ninguna característica técnica de la composición. Se le recuerda al solicitante que una composición se caracteriza por sus componentes específicos y sus proporciones de combinación.

En consecuencia el capítulo reivindicatorio no cumple con el requisito de concisión y sustento en la descripción de acuerdo al art. 30 de la Decisión 486.

4. Reivindicaciones relativas a un uso o a un segundo uso (artículos 14 y 21 D 486)

La reivindicación 13 hace referencia al uso de una sal de nitrato iónica. Lo cual de acuerdo con el artículo 14 no es patentable pues no corresponde a una invención de producto ni de procedimiento.

Asimismo el método de la reivindicación 12 hace referencia simplemente al uso de la composición pesticida de interés para el control selectivo de plagas en cultivos de plantas útiles. Es evidente que la llamada etapa de "el tratamiento" corresponde a la forma de usar la composición. Por lo tanto la reivindicación 12 no es patentable a partir de lo dispuesto en la Decisión 486.

Se le aclara al solicitante que un procedimiento cuya única etapa es una aplicación corresponde tan solo a una aplicación, y una aplicación es un uso.

5. Determinación del Estado de la Técnica

Considerando que la fecha de la prioridad de la solicitud internacional PCT es 2003-12-05, se realizó la búsqueda en el estado de la técnica y se encontraron los documentos relacionados a continuación, que pueden afectar la patentabilidad del objeto de la presente solicitud:

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Nº	Documento	Título	Fecha de publicación
D1	US5416061	Herbicidal combinations of bromoxynil with selected 2-benzoylcyclohexane 1,3-diones	1995-05-16
D2	WO99/07918	Method of inhibiting corrosion of flux-treated metal surfaces	1999-02-18

El documento D1 divulga composiciones herbicidas que comprenden (a) bromoxinil y (b) 2-benzoilciclohexano 1,3 dionas.

El documento D2 divulga un método para inhibir la corrosión de superficies metálicas.

6. Análisis de patentabilidad (artículo 14 D486)

6.1. Nivel Inventivo (artículo 18 D486)

La solicitud de patente en estudio presenta un concentrado pesticida que comprende:

- 2-85% en peso de agua.
- 5-90% en peso de al menos un pesticida.
- Una cantidad de aditivo de sal de nitrato iónica, efectiva para reducir la corrosión de superficies metálicas.
- Optativamente, otros auxiliares de formulación.

En donde la relación del componente c) al componente b) es inferior ó igual a 0.3:1.

El documento D1 divulga composiciones herbicidas que comprenden (a) bromoxinil y (b) 2-benzoilciclohexano 1,3 dionas. Dichas composiciones herbicidas pueden ser formuladas en solución acuosa (columna 17 líneas 40-45) y pueden contener entre otros aditivos de formulación, un inhibidor de la corrosión (columna 18, líneas 5-6).

Al comparar el concentrado de esta solicitud con las composiciones de D1 se observa que dicho concentrado contiene una sal de nitrato.

El efecto técnico que produce la presencia de una sal de nitrato en la formulación es la inhibición de la corrosión en superficies metálicas.

El problema técnico objetivo sería entonces como modificar las composiciones de D1 para evitar la corrosión de las superficies metálicas que tienen contacto con esas formulaciones de base acuosa.

En contraste, el documento D2 enseña claramente que una sal inorgánica de nitrato (NaNO_3) es especialmente útil como inhibidor de la corrosión en superficies metálicas que tienen contacto con fluidos acuosos (pagina 6 líneas 11-14 y resumen)

En consecuencia, para un técnico medio en la materia teniendo en cuenta las enseñanzas del estado de la técnica en su totalidad, sería obvio incluir el inhibidor de la corrosión de D2, justamente para inhibir la corrosión de las superficies metálicas.

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Por lo tanto el concentrado de esta solicitud es una alternativa obvia para un técnico medio en la materia, no provoco un efecto técnico inesperado ó sorprendente y carece nivel inventivo.

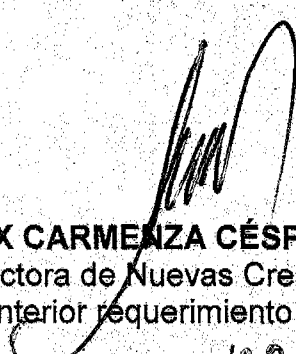
7. Conclusión

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	US5416061	1-11	Nivel Inventivo
D2	WO99/07918	1-11	Nivel Inventivo

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

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


ALIX CARMENZA CÉSPEDES DE VERGEL

Directora de Nuevas Creaciones (C)

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

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CONCEPTO TÉCNICO No. 3994

EXAMINADOR TÉCNICO

Código No.202085