

**CASTELLANOS & CO.**  
**A B O G A D O S**  
Calle 94 A No. 7 A - 09  
Bogotá, D.C., COLOMBIA

Señora  
**Jefe de la División de Nuevas Creaciones**  
**Superintendencia de Industria y Comercio**  
**Ministerio de Desarrollo Económico**  
E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



**No. 02-026312- -00009-0000**

Fecha: 2007-11-27 14:24:44 Dep. 2020 NUECREACIONE  
Tra. 2 PATENTES Eve: 1 REGDEPOSITO  
Act. 444 RESPUESTAREQUE Folios: 7

Ref.: Expediente No. 02.026.312

Solicitud de Patente de Invención para: **COMPOSICIÓN ACUOSA QUE  
COMPRENDE UNA SAL DE PARAQUAT Y ALGINATO**  
Solicitante: **SYNGENTA LIMITED**

### **RESPUESTA AL EXAMEN DE FONDO**

**MARGARITA CASTELLANOS ABONDANO**, mayor de edad, identificada y domiciliada como aparece al pie de mi firma, atentamente me permito presentar respuesta al oficio No. 10304, notificado por fijación en lista el 30 de agosto de 2007 correspondiente al examen de fondo, estando dentro del término legal en los siguientes términos:

#### **1. Claridad de la solicitud**

Argumenta su despacho que aunque no se aceptaron las modificaciones al capítulo reivindicatorio, cabe anotar que si bien fueron solventados los problemas de claridad no es posible establecer la unidad de invención.

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Con el fin de superar las objeciones por claridad y unidad de invención, presento nuevo capítulo reivindicatorio compuesto por 7 reivindicaciones donde se han realizado las siguientes modificaciones:

El pliego reivindicatorio está limitado a una composición que contiene una sal de paraquat y alginato siguiendo claramente la sugerencia del señor examinador en cuanto a definir claramente la composición reivindicada. Así mismo, no se hace mención a la sal de diquat ni a la mezcla de la sal de diquat y paraquat los cuales le restaban claridad al capítulo reivindicatorio por cuanto no había unidad de invención.

Adicionalmente, en el nuevo capítulo reivindicatorio se eliminaron los auxiliares de formulación entre ellos trisilicato de magnesio, tensioactivo y el polímero adicional de gel con el fin de hacer mas clara la composición reivindicada. Además se ha especificado que la composición contiene un emético y un purgante (cada uno de ellos claramente definidos) superando de esta forma la objeción efectuada por el examinador.

Por otra parte, pongo de presente a su Despacho que la composición de paraquat ahora reivindicada se encuentra debidamente sustentada en la descripción (ejemplos 1 a 7).

"Argumenta su Despacho que en la reivindicación 7 se presenta una clasificación para el alginato como "rico en M" el cual es poco preciso".

Con el fin de superar la presente objeción, el término rico en M se ha eliminado del capítulo reivindicatorio.

"Por otro lado su despacho objeta el capítulo reivindicatorio por cuanto la composición debería definirse según los compuestos de la formulación y las proporciones en la que se encuentran".

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Esta objeción debe tenerse como superada toda vez que en el nuevo capítulo reivindicatorio la composición ha sido definida en función de sus componentes así como las proporciones de los mismos.

"Adicionalmente su Despacho objeta el método para preparar la composición toda vez que el mismo no se encuentra claramente definido. Igualmente sucede con el proceso para matar o controlar especies ya que el mismo no se encuentra definido en función de las etapas y condiciones".

Con el fin de superar las objeciones sobre las reivindicaciones de método, las mismas se han eliminado del capítulo reivindicatorio.

Por su parte, las reivindicaciones relacionadas con usos han sido eliminadas del capítulo reivindicatorio. Por lo tanto, las objeciones que existían sobre las mismas se deben dar por superadas.

Con el fin de superar la objeción acerca del título el mismo ha sido modificado como sigue:

**"Composición acuosa que comprende una sal de paraquat y alginato"**

## **2. Unidad de Invención**

"Argumenta se Despacho que si se pretende proteger una composición se tendrían varias composiciones diferentes ya que una composición contendría la sal de paraquat, otra composición una sal de diquat y una tercera composición tendría una mezcla de las dos sales".

Con las modificaciones realizadas al capítulo reivindicatorio queda claro que la invención es clara y constituye un único concepto inventivo toda vez que la reivindicación 1 se encuentra dirigida a una **composición de paraquat** y **alginato** y las proporciones de cada uno de los componentes de la formulación han sido claramente definidos.

**CASTELLANOS & CO.**

ABOGADOS  
Calle 94 A No. 7 A - 09  
Bogotá, D.C., COLOMBIA

Cumplido así con lo dispuesto, respetuosamente solicito a Ud., se otorgue el privilegio de patente de invención a la presente solicitud toda vez que las objeciones hechas por su Despacho han sido superadas.

**3. Anexos**

- Nuevo capítulo reivindicatorio
- Formato de Modificaciones
- Recibo de Pago

De la Señora Jefe,

*Margarita Castellanos Abondano*  
**Margarita Castellanos Abondano**

C.C. No. **39.779.654** de Usaquén

T.P.A. No. **70819** del C. Sup. de la Judicatura

Calle 94 A No. 7 A - 09

Teléfonos: 610 74 20

Bogotá, D.C.,

27 NOV. 2002

G/USER/DEPARTAMENTO DE PATENTES/PATENTES/8/P836/MEMORIAL DE FONDO

FORMULARIO ÚNICO DE CORRECCIONES Y MODIFICACIONES

①

SOLICITUD DE:

☐

Corrección de Error Material

☒

Modificación a una solicitud

②

SOLICITANTE

Nombre: SYNGENTA LIMITED

Dirección: European Regional Center  
Priestley Road  
Surrey Research Park, Guilford  
Surrey GU2 7YH  
Reino Unido

Domicilio: Surrey Research Park, Guilford  
Surrey GU2 7YH  
Reino Unido

Lugar de Constitución: Reino Unido

Teléfono:

Fax:

E-mail:

IDENTIFICACIÓN

C.C.

☐

NIT

☐

C.E.

☐

Otro

☐

Cual

Número

③

REPRESENTANTE  
O APODERADO

Nombre: MARGARITA CASTELLANOS A.

Dirección: CALLE 94A No. 7A-09

Teléfono: 610 74 20 Fax: 610 07 06

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IDENTIFICACIÓN

C.C.

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NIT

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C.E.

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Otro

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Cual

Número

39'779.654

TPA

70.819

④

Número de Expediente:

02.026.312

⑤

Descripción de la corrección o modificación solicitada:

Presento nuevo pliego reivindicatorio con 7 reivindicaciones sobre el cual solicito de efectúe el examen de patentabilidad de la solicitud.

⑥

Comprobante de pago No.

07-96,008

Fecha

26 de noviembre de 2007

⑦

Anexos:

☒

Comprobante de pago de la tasa.

☐

Poderes si fuere el caso, junto con la sustitución de los mismos a mi favor.

☐

Documento que acredita la existencia y representación legal de las partes, cuando sean personas jurídicas

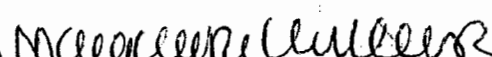
☒

Nuevo capítulo reivindicatorio

⑧

NOMBRE MARGARITA CASTELLANOS A.

FIRMA

  
CC 39'779.654 Usaquén - TPA 70.819 CSJ

167  
767

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 07 - 96,008  
FECHA : NOVIEMBRE 26 DE 2007



\*\*\*\*\* CONSIGNACION \*\*\*\*\*

| DEPOSITANTE        | TIPO PAGO    | BANCO         | CUENTA       | No. PAGO | FECHA PGO  | Vr. PAGO     |
|--------------------|--------------|---------------|--------------|----------|------------|--------------|
| ALVARO CASTELLANOS | CONSIGNACION | BANCO POPULAR | 050-00110-6. | 71033165 | 26/11/2007 | 2,273,000.00 |

\*\*\*\*\* C O N C E P T O \*\*\*\*\*

| CANT. | RENTISTICO  | CONCEPTO                       | TOTAL CONCEPTO |
|-------|-------------|--------------------------------|----------------|
| 1     | 50005-01-03 | CAMBIO DE MODALIDAD Y MODIFICA |                |
|       |             | 12 MARCAS Y LEMAS COMERCIALES  | 99,000.00      |
|       |             | TOTAL :                        | \$ 99,000.00   |

NOVENTA Y NUEVE MIL PESOS

RESPONSABLE : \_\_\_\_\_

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. \_\_\_\_\_

## REIVINDICACIONES

1. Una composición acuosa que comprende ambos, una sal de paraquat en una cantidad desde 50 a 400 g/l de la composición, y un alginato, en una cantidad desde 3 a 50 g/l de la composición, comprendiendo además la composición un emético y un purgante de modo tal que el efecto inductor de gelificación por pH tiene lugar al pH ácido del jugo gástrico humano.
2. Una composición acuosa de acuerdo con la reivindicación 1 en donde el alginato tiene una viscosidad en solución acuosa al 1 % como aquí se define desde 2 a 1000 mPas.
3. Una composición acuosa de acuerdo con la reivindicación 2 en donde el alginato tiene una viscosidad en solución acuosa al 1 % como aquí se define desde 20 a 400 mPas.
4. Una composición acuosa de acuerdo con la reivindicación 1 en donde el contenido de calcio del alginato es menor que 1%.
5. Una composición acuosa de acuerdo con la reivindicación 1 en donde el pH se ajusta ente 4 y 9.
6. Una composición acuosa de acuerdo con la reivindicación 1 en donde el emético es 2-amino-6-metil-5-oxo-4-*n*-propil-4,5-dihidro-[1,2,4]triazolo[1,5-*a*]-pirimidina.
7. Una composición acuosa de acuerdo con la reivindicación 1 en donde el purgante es sulfato de magnesio.

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 467 529 A2**

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~~169~~  
169

(12)

## EUROPEAN PATENT APPLICATION

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(51) Int. Cl.<sup>5</sup>: **A01N 25/32, A01N 43/40,  
A01N 43/90**

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(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

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(54) **Herbicidal compositions.**

(57) A herbicidal composition, comprising preferably an aqueous solution of a salt of paraquat or diquat, or a mixture thereof, in admixture with a gelling agent that will gel at the pH of human gastric juice, (e.g. magnesium silicate), and further comprising (1) an emetic, (e.g. a triazolopyrimidine emetic) or (2) a purgative (e.g. magnesium sulphate), or (3) both an emetic and a purgative.

In the event of ingestion of the composition, these additives act synergistically to reduce absorption of bipyridylium compound from the gastrointestinal tract into the bloodstream, and thereby reduce the oral toxicity of the composition.

**EP 0 467 529 A2**

This invention relates to herbicidal compositions containing a herbicidal bipyridylum diquatary salt as an active ingredient.

Various herbicidal bipyridylum diquatary salts are described in United Kingdom Patent Specification No. 785732, 813531 and 813532. Certain of these compounds (e.g. salts of paraquat and diquat; the chemical identity of these compounds is given later in this specification) are in widespread use in agriculture, and are manufactured for sale in the form of concentrated aqueous solutions. When required for use, these concentrated solutions are diluted with water to form a solution which is then sprayed upon unwanted plants. When used with due care, and in accordance with recommended procedures, the concentrated aqueous solutions present no hazard. However, hazards may develop if adherence to the recommended handling practices is not maintained. Thus it may happen that an operator may decant some of the concentrate into a domestic container such as a beverage bottle for subsequent use in his own garden at home. The hazard associated with such a practice is of course that a child or incautious adult coming upon the bottle may swallow some of the contents, with possible serious consequences.

Various methods have been proposed to reduce the likelihood of accidental swallowing of concentrated solutions of bipyridylum diquatary salts in the circumstances described above. These include the inclusion of an odourant in the concentrate as a warning (see UK Patents 1406881 and 1570981), the inclusion of a water-soluble blue dye, and the inclusion of a substance to convert the concentrate into a thixotropic gel (see UK Patent 1395502).

Another approach to reducing the possibility of harmful effects following the ingestion of a bipyridylum salt concentrate has been to include an emetic in the concentrate, so that the concentrate will be removed by vomiting shortly after its ingestion (see UK Patent 1507407). A further approach has been to formulate the bipyridylum diquatary salt as a multiple emulsion, as proposed in published European Patent Application No. 276911. In addition to methods of formulating bipyridylum herbicides so as to reduce the likelihood of accidental ingestion, a variety of methods has been proposed for formulating bipyridylum herbicides so as to improve their suitability for particular applications. Thus, it has been proposed to formulate an aqueous solution of paraquat as an invert emulsion in oil (see United States Patent 4115098) in order to reduce drift and evaporation of the droplets of spray when the paraquat is applied as a herbicide.

According to the present invention, there is provided a herbicidal composition comprising a salt of paraquat or diquat, or a mixture thereof, in admixture with a gelling agent that will gel at the pH of human gastric juice, and further comprising (1) an emetic, or (2) a purgative, or (3) both an emetic and a purgative.

The compositions may be solid or liquid.

According to a preferred aspect of the present invention, there is provided a herbicidal composition comprising an aqueous solution of a salt of paraquat or diquat, or a mixture thereof, in admixture with a gelling agent that will gel at the pH of human gastric juice, and an emetic.

Preferably the aqueous compositions contain 50, and more preferably, 100 grams per litre or more of paraquat or diquat, or a mixture thereof.

The aqueous compositions may contain, for example, 200 grams or more per litre of paraquat or diquat or a mixture thereof.

The aqueous compositions of the invention may further comprise a purgative. They may also comprise a suspending agent to assist in keeping the gelling agent evenly dispersed throughout the composition during storage and transport.

If a quantity of a composition according to the invention is ingested, the acidity of the gastric juice (which ranges from pH1.5 to pH3.5) will cause the composition to gel in the stomach. Increasing the viscosity of the gastric contents slows down the rate of gastric emptying. The bipyridylum herbicide will consequently be trapped in the gel, and its movement from the stomach and into the absorptive small intestine will be impeded. Ideally, the gelling agent is one which will also reduce gastric acidity and therefore reduce local irritation of the gastric mucosal lining. The emetic present in the composition is absorbed rapidly and will in a short time cause expulsion of the gel containing the bipyridylum herbicide by vomiting, thereby preventing the ingested herbicide from moving further down the gastrointestinal tract, where absorption of the bipyridylum compound would otherwise take place. In preferred compositions according to the invention, a purgative is present in the composition, to assist in removing any non-absorbed bipyridylum herbicide which has passed from the stomach into the small intestine despite the action of the emetic. In the event of a bipyridylum composition according to the invention being ingested, the combined effects of the gelling agent, emetic, and when included, the purgative, will be to substantially reduce the absorption of the bipyridylum compound from the gastrointestinal tract into the bloodstream, and thereby to reduce the oral toxicity of the concentrate.

Paraquat is the common name of the 1,1'-dimethyl-4,4'-bipyridylum cation, having the structure (I) (see formula sheet).

Diquat is the common name of the 1,1'-ethylene-2,2'-bipyridylium cation, having the structure (II) (see formula sheet).

Salts of paraquat and diquat necessarily contain anions carrying sufficient negative charges to balance the two positive charges on the bipyridylium nucleus.

5 Since the characteristic herbicidal effect of a bipyridylium quaternary cation is independent of the nature of the associated anion, the choice of the anion is a matter of convenience, depending, for example, on cost. Preferably the anion is one which gives rise to a salt of convenient water solubility. Examples of anions, which may be mono- or poly-valent, include acetate, benzenesulphonate, benzoate, bromide, butyrate, chloride, citrate, fluorosilicate, fumarate, fluoroborate, iodide, lactate, malate, maleate, methylsulphate, nitrate, propionate, phosphate, salicylate, succinate, sulphate, thiocyanate, tartrate, and p-toluenesulphonate. The salt of the herbicidal bipyridylium cation may be formed from a number of similar anions or mixtures of different ones. A salt having any particular desired anion may be prepared either by direct synthesis from reactants which include the desired anion, or by exchanging the anion of a previously prepared salt of the preferred anion by methods well known in the art, for example by passage of a solution of the previously prepared salt through an ion-exchange resin. For reasons of convenience and economy, paraquat is normally manufactured and sold as paraquat dichloride while diquat is manufactured and sold as diquat dibromide.

Since the characteristic herbicidal activity of a salt of a herbicidal bipyridylium quaternary cation resides in the cation only, it is customary to quote concentrations of active ingredient and rates of application in terms of the amount of bipyridylium quaternary cation used. Application rates and concentrations quoted in this specification therefore relate to the amount of bipyridylium quaternary cation unless otherwise stated.

Preferably, aqueous compositions according to the invention contain at least 50 grams per litre of paraquat or diquat or mixtures thereof. The compositions may contain 100 grams per litre or more of paraquat or diquat or mixtures thereof. Compositions containing 200 grams or more per litre, for example 300 grams per litre, may be prepared.

The gelling agent is preferably magnesium silicate, although other gelling agents may be used.

As commercially manufactured, (e.g. by reaction of sodium silicate with magnesium sulphate), magnesium silicate has a somewhat variable composition; thus, the ratio of silica ( $\text{SiO}_2$ ) to magnesium oxide ( $\text{MgO}$ ) in commercial technical grades of this material may range for example from about 3.3 to 1.5. Typical chemical analyses for two commercial technical grades of magnesium silicate (designated PDM15 and PDM 33) are given below.

|                                           | PDM 33 | PDM 15     |
|-------------------------------------------|--------|------------|
| 35 MgO                                    | 12-13% | 22.6-24.6% |
| $\text{SiO}_2$                            | 61-65% | 49.5-53.5% |
| Molecular ratio $\text{SiO}_2/\text{MgO}$ | ~ 3.3  | ~ 1.5      |
| 40 Fe                                     | 0.03%  | 0.03%      |
| $\text{SO}_4$                             | 2.5%   | 1.5%       |
| Loss in weight on ignition at 900°C       | 18-22% | 20-30%     |

45 In preparing herbicidal compositions according to the present invention, it is preferred to use a grade of magnesium silicate which has a relatively high magnesium oxide content, for example magnesium silicate approximating to the composition  $2\text{MgO} \cdot 3\text{SiO}_2$ . Magnesium silicate of this composition is often designated as magnesium silicate, and is so designated throughout this specification. Suitably purified and sterilised grades of this material are used pharmaceutically as an antacid.

50 Magnesium trisilicate is also known as magnesium mesotrisilicate. It is described in the Merck Index (Ninth Edition, published in 1976 by Merck and Co., Inc., Rahway, New Jersey, USA; see entry No. 5514 on pages 738-739) as an odourless, tasteless, slightly hygroscopic powder, having the chemical formula  $\text{Mg}_2\text{Si}_3\text{O}_8$ . It is usually hydrated to some extent. According to the British Pharmacopoeia, 1988, volume 1, page 348 (published by H M Stationery Office, London), magnesium trisilicate is a hydrated magnesium silicate of the approximate composition  $2\text{MgO} \cdot 3\text{SiO}_2$  containing water of crystallisation. The pharmaceutical grade contains not less than the equivalent of 29.0% of  $\text{MgO}$ , and not less than the equivalent of 65.0% of  $\text{SiO}_2$ , both calculated with reference to the substance after ignition at 900°C. The use of magnesium trisilicate as a gelling agent in the compositions of the present invention has the advantage that it reduces

gastric acidity, and thereby, as mentioned above, reduces local irritation of the gastric mucosal lining. Magnesium trisilicate and the silicon dioxide gel produced in the stomach both have adsorbent properties. This reduces the bioavailability of bipyridylum salts when they are in concentrated solution. The magnesium trisilicate is preferably present in a concentration of from 10 to 400 grams per litre of the composition, and more preferably in a concentration of from 10 - 100 grams per litre. Since magnesium trisilicate is insoluble in water, it may tend to settle to the bottom of the container in which the composition is stored. Liquid compositions of the invention containing magnesium trisilicate therefore preferably also comprise a suspending agent, to assist in keeping the magnesium trisilicate dispersed homogeneously throughout the composition. Examples of suitable suspending agents include bacterial polysaccharides, for example the material known as xanthan gum, and in particular the xanthan gum sold under the trade name "KELZAN". Other suitable suspending agents include alginates. The suspending agents may be present in a concentration of for example from 0.01 gram to 100 grams per litre of the composition.

A variety of known emetics may be used in the compositions of the invention. However, preferred emetics are those compounds disclosed in UK Patent No. 1507407 for use in formulations of bipyridylum herbicides, and a particularly preferred emetic is 2-amino-6-methyl-5-oxo-4-n-propyl-4,5-dihydro-5-triazolo-[1,5-a]-pyrimidine, having the structural formula (A) (see formula sheet).

The amount of emetic used in the composition will vary depending upon the particular type of emetic used, but when an emetic of the class disclosed in UK Patent No. 1507407 is used, the concentration of emetic is preferably from 0.1 to 5 grams per litre of the composition.

For a composition containing 200 grams per litre of bipyridylum compound, a concentration of 1.5 to 2.0 grams per litre of emetic is preferred.

When the composition of the invention contain a purgative, this is preferably magnesium sulphate. The concentration of magnesium sulphate is preferably from 10 to 400 grams per litre of the composition, and more preferably from 10 to 100 grams per litre.

The compositions of the invention may also contain further ingredients for example one or more surface-active agents.

Surface-active agents may be cationic, non-ionic or anionic. Generally speaking cationic and non-ionic surface-active agents are preferred to anionic surface-active agents for use in the compositions of the invention, since the latter may interact undesirably with the bipyridylum quaternary salt in the compositions, but anionic surface-active agents may be used where such interactions do not occur. Examples of non-ionic surface-active agents for use in the compositions of the invention include the condensation products of ethylene oxide with alkyl phenols such as octylphenol, nonylphenol and octylcresol for example the condensation product of p-nonylphenol with 8 molar proportions with of ethylene oxide sold under the trade name of Synperonic NP8. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, for example sorbitan monolaurate; the condensation products of the said partial esters with ethylene oxide; and the lecithins. Examples of cationic surface-active agents include quaternary salts and condensates of ethylene oxide with amines, for example the substances sold under the Trade Mark "Ethomeen", "Ethoduomeen", "Duoquad" and "Arquad". A particular example comprises the condensate of a C<sub>13</sub> to C<sub>15</sub> mixture of synthetic primary amines with 15 molar proportions of ethylene oxide sold under the trade name "Synprolam" 35x15. The proportion of surface-active agent present in the aqueous compositions of the invention is not highly critical and a suitable proportion may readily be decided upon by a person skilled in the formulation art without excessive experimentation. However by way of illustration an amount of 50 to 100 grams per litre of the composition is usually suitable; although more or less may be used depending upon the particular composition. The composition of the invention may also contain an odourant, such as a pyridine derivative, as described in UK Patent No. 1406881, or n-valeric acid. The compositions may also comprise a pigment or a dye to give them a distinctive colour.

In greenhouse tests, compositions according to the invention containing paraquat have been found to be equivalent in herbicidal effect to commercial aqueous formulations of paraquat, the two types of composition being applied at the same rate of application of active ingredient.

Aqueous compositions according to the invention are readily prepared by adding the various constituents of the formulation to an aqueous solution of a salt of paraquat or diquat or a mixture thereof, with suitable agitation.

Solid compositions according to the invention include compositions of the kind disclosed in UK Patent Specification No. 1,086,939, which describes a process of mixing a hydrate-forming salt (e.g. magnesium sulphate) with an aqueous solution of a bipyridylum herbicide in proportions such that the hydrate-forming salt combines with sufficient of the water present to give a solid composition. Solid compositions according to the present invention may be prepared by additionally including in the mixing process a gelling agent (e.g. magnesium trisilicate) and an emetic, in proportions in similar to those used in the aqueous

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |           |                                                                                                                                         |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|-----------------------------------------------------------------------------------------------------------------------------------------|
| <b>(51) International Patent Classification<sup>4</sup> :</b><br><b>A01N 25/32, 25/14</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 87/ 02864</b><br><b>(43) International Publication Date:</b> 21 May 1987 (21.05.87) |
| <b>(21) International Application Number:</b> PCT/JP85/00630<br><b>(22) International Filing Date:</b> 12 November 1985 (12.11.85)<br><b>(71) Applicant:</b> SDS BIOTECH K.K. [JP/JP]; 12-7, Higashi Shinbashi 2-chome, Minato-ku, Tokyo 105 (JP).<br><b>(72) Inventors:</b> YAMASHITA, Kazuhiro ; YOSHIDA, Mamoru ; SDS Biotech K.K., Tokyo Kenkyusho, 24-25, Tamagawa 2-chome, Ota-ku, Tokyo 143 (JP).<br><b>(74) Agents:</b> AOKI, Akira et al.; A. Aoki & Associates, Seiko Toranomon Bldg., 8-10, Toranomon 1-chome, Minato-ku, Tokyo 105 (JP).<br><b>(81) Designated States:</b> AU, BR, DK, HU, IT (European patent), NL (European patent), SU. |           | <b>Published</b><br><i>With international search report.</i>                                                                            |
| <b>(54) Title:</b> CONTRADEGLUTITIOUS SOLID HERBICIDAL COMPOSITION<br><br><b>(57) Abstract</b><br><br>A contradeglutitious solid herbicidal composition comprising a 1,1'-dimethyl-4,4'-dipyridylum salt and a thickening agent. This composition is difficult to swallow in its original form or even when diluted in a glass of water. The composition does not impair the inherent herbicidal effects and applicability of paraquat.                                                                                                                                                                                                                |           |                                                                                                                                         |

DESCRIPTION

## TITLE OF THE INVENTION

CONTRADEGLUTITIOUS SOLID HERBICIDAL COMPOSITION

## BACKGROUND OF THE INVENTION

The present invention relates to a contra-  
5 deglutitious solid herbicidal composition (i.e., a  
herbicidal composition not easy to swallow). More  
specifically, it relates to a contra DEGLUTITIOUS solid  
herbicidal composition containing, as a herbicidal  
agent, a 1,1'-dimethyl-4,4'-dipyridylium salt (i.e.,  
10 so-called "paraquat"), which is not easily swallowed  
even if such a paraquat solution is accidentally or  
intentionally drunk.

The importance of herbicides or pesticides  
in modern agriculture is widely recognized and many  
15 herbicides or pesticides are in practical use.  
Herbicides or pesticides practically used must be  
registered, after being subjected to a severe examination  
including the toxicity and safety thereof based on the  
laws and regulations concerned. Accordingly, as long as  
20 herbicides or pesticides are properly used according to  
instructions for use, they will not harm the human body  
in any way. However, the present status is such that  
toxic or poisonous accidents caused by a portion of  
herbicides or pesticides still occur in spite of the  
25 fact that the proper handling of herbicides or pesticides  
and the preventing of injury thereby to the human body  
has been taught and the dangers of improper usage have  
been widely announced for a long time. In particular, a  
herbicide, paraquat, is widely used because of the  
30 strong herbicidal effect and easy applicability thereof,  
and quite a large number of toxic or poisonous accidents  
have been caused by the accidental or intentional  
drinking of paraquat despite clear indications of its  
toxicity. This is because paraquat has very strong  
35 acute toxicity and is commercially available in the form

of an aqueous solution having a relatively high concentration.

Paraquat is generally marketed as an about 20% to 30% aqueous solution. When used, the raw paraquat solution is diluted 300 to 1500 times with water and the resultant diluted paraquat solution is generally sprayed as a weed-killer in an amount of 100 to 150 liters per 10 are (i.e., 100 m<sup>2</sup>). The oral acute toxicity of paraquat is an LD<sub>50</sub> of 166 to 217 mg/kg (rat) and it is reported in "Kyukyu Igaku" 4(4), p 399 (1980) that the lethal dose of paraquat for humans is approximately 15 ml of the 20% aqueous solution. On the other hand, it is reported in "Gekkan Yakuji" 25(8), p 147 (1983) that an average amount drunk in one mouthful by an adult human is generally approximately 40 ml. This means that, if a commercially available paraquat solution is accidentally or intentionally drunk, a mouthful of the paraquat solution is sufficient to be lethal to a human.

Various attempts have been made to prevent accidental toxic or poisonous injury caused by paraquat. For example, odorants or colorants are mixed into the paraquat solutions to prevent accidental drinking by giving it an unpleasant odor or color. However, this is not effective for infants or against intentional drinking. Furthermore, the inclusion of nauseants in the paraquat solutions has been proposed, to rapidly remove the mistakenly drunk paraquat from the stomach and other digestive system prior to the absorbance of paraquat into the body therethrough. However, it is extremely unfortunate that, at present, once paraquat is swallowed, a reliable and effective curing or treatment method is not available, although this depends upon the amount swallowed, even if the paraquat is vomitted at an early stage.

Consequently, although various attempts have been made to solve the above-mentioned problems, an appropriate and effective means has not, as yet, been

found. In order to prevent toxic or poisonous accidents caused by the oral intake of paraquat, it is thought that the concentration of commercially available paraquat should be decreased so that a lethal amount is not reached unless a relatively large amount of a paraquat solution is drunk. However, this causes disadvantages in the transportation and storage of paraquat solutions and also impairs the inherent easy handling characteristics of paraquat. On the other hand, it is considered that, when paraquat is marketed in the form of a solid instead of an aqueous solution, the paraquat becomes difficult to drink, toxic or poisonous injuries caused by the accidental intake of paraquat can be prevented, and, furthermore, the transportation and storage thereof are convenient. However, since paraquat is completely soluble in water, an aqueous solution containing a lethal amount of paraquat is easily prepared from such solid paraquat with a mouthful of water, it would be difficult to prevent to take the poison with suicidal intent.

#### SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to eliminate the above-mentioned disadvantages of paraquat and to provide a contradeplutitious solid herbicidal composition capable of effectively preventing the occurrence of accidents or injuries from acute poisoning caused by an accidental or intentional intake of paraquat, without impairing the essential characteristics, e.g., strong herbicidal effects and easy applicability, of paraquat.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a contradeplutitious solid herbicidal composition comprising a 1,1'-dimethyl-4,4'-dipyridylum salt and a thickening agent.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, since the herbicidal composition is in a solid form and contains a thickening agent, it is difficult to swallow in the solid form itself and, if an amount of the composition corresponding to a lethal dose to human beings is dissolved in a glass of water, only a non-fluidizable mixture, which is difficult to swallow, is obtained. Of course, the present solid herbicidal composition can be changed to an aqueous solution by diluting the composition with a large amount of water. However, since the paraquat concentration of this diluted solution is very low, a lethal amount cannot be ingested unless a remarkably large amount of the diluted solution is drunk. This is practically difficult and the effects of nausea can be utilized to decrease the likelihood of death from such ingestion. Furthermore, since the present solid herbicidal composition can be stored and transported in glass and plastic vessels, and since the present solid herbicidal composition can be used on-site by diluting with water, there is no substantial difference between the present solid herbicidal composition and conventional commercially available paraquat solutions in the transportation, handling, and applicability thereof. When diluting the present solid herbicidal composition with a large amount of water for use on-site, the present solid herbicidal composition becomes a low viscosity solution suitable for spraying.

Furthermore, the solid herbicidal composition according to the present invention may optionally contain, in addition to the essential paraquat and thickening agent, various conventional ingredients such as colorants, odorants, and nauseaants, to further improve the safety thereof. In addition, surfactants and other herbicidal active components also can be included in the present herbicidal composition to improve the herbicidal effects and the applicability of the herbicidal composition.

The paraquat usable in the present herbicidal composition is preferably in the form of a solid. Accordingly, 1,1'-dimethyl-4,4'-dipyridylium salts (e.g., dichloride, dibromide, and bismethylsulfate or the complex salts with, for example, manganese, iron, urea, thiourea, p-aminophenol, catechol) in the form of crystals can be directly mixed with the thickening agent. However, the industrially or commercially available paraquat solutions also can be used in the preparation of the present solid herbicidal composition by adding a water-absorbing inorganic fine powder to form an apparently water-free fluidizable solid paraquat. Any water-absorbing inorganic fine powder can be used for this purpose so long as the herbicidal effects of the paraquat and the characteristics of the thickening agents are not adversely affected. Examples of such water-absorbing inorganic fine powders are white carbon, diatomaceous earth, finely divided calcium silicate, perlite, calcined kaoline, and zeolite. These can be used alone or in any mixture thereof. There are no critical limitations to the addition amount of the water-absorbing inorganic fine powder, as long as the paraquat solution can be solidified. For example, in the case of white carbon, an equal amount of the powder can be mixed with 10 times the amount of the water contained in the aqueous paraquat solution.

There are no critical limitations to the paraquat concentration of the present solid herbicidal compositions. However, when the paraquat concentration is too low, only a small dilution ratio of the composition with water is required to obtain the desired concentration when spraying on-site and, therefore, spraying tends to become difficult from the standpoint of both the viscosity and the spraying amount, and the efficiency of the transportation and storage also tends to be decreased. On the other hand, when the paraquat concentration in the present herbicidal composition is too

high, the above-mentioned problems do not arise but the allowable safety range tends to become small from the point of view of preventing the possible occurrence of toxic or poisonous accidents.

- 5 For these reasons, the practically preferable concentration range of the paraquat in the present herbicidal compositions is from about 5% by weight to 40% by weight.

10 The thickening agents usable in the present invention are those which are capable of increasing the viscosity or forming the gel with the addition of a relatively small amount (e.g., 300 ml or less) of water to the solid herbicidal composition at an ambient temperature in a short period of time. There are no  
15 specific limitations to the types of the thickening agents as long as the above-mentioned requirements are fulfilled. Various natural and synthetic thickening agents can be used in the present invention. Typical examples of such thickening agents are alginic acid  
20 salts, propylene glycol alginates; carrageenan, guar gum, modified guar gum, xanthan gum, modified xanthan gum, carboxymethyl cellulose salts, methyl cellulose, hydroxyalkyl cellulose, pectine, locust bean gum, carboxymethyl starch salts, pullulan, polyvinyl alcohol,  
25 polyvinyl pyrrolidone, polyacrylic acid salts, and polyacryl amide. These thickening agents may be used alone or in any mixture thereof. Furthermore, various conventional acids or salts also may be used in the present herbicidal compositions to further improve the  
30 gellation or thickening characteristics of the present solid herbicidal composition. The addition of inorganic salts to the present herbicidal composition can further improve the gellation properties of the present herbicidal compositions.

- 35 There are no definite concentrations of the thickening agents in the present herbicidal compositions since the concentrations largely depend upon the type of

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO  
DIVISI3N DE NUEVAS CREACIONES

2020  
Bogot3, D.C., (10 de Diciembre del 2007)

Abogado  
Margarita Castellanos Abondano  
(Apoderado)  
Solicitante: SYNGENTA LIMITED.

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|--------|------------|----------|
| ASUNTO | Radicaci3n | 02-26312 |
|        | Tr3mite    | 002      |
|        | Evento     | 001      |
|        | Actuaci3n  | 430      |
|        | Oficio     | 16775    |
|        | Folios     | 004      |

|                                 |                                     |                               |                          |
|---------------------------------|-------------------------------------|-------------------------------|--------------------------|
| Patente de Invenci3n            | <input checked="" type="checkbox"/> | Patente de Modelo de Utilidad | <input type="checkbox"/> |
| V3a Nacional                    | <input checked="" type="checkbox"/> |                               |                          |
| V3a PCT (fase nacional)         | <input type="checkbox"/>            | Cap.I                         | <input type="checkbox"/> |
|                                 |                                     | Cap. II                       | <input type="checkbox"/> |
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| Fecha de Presentaci3n Internal. | <hr/>                               |                               |                          |

Como resultado del examen de fondo, realizado con fundamento en el art3culo 45 de la Decisi3n 486 de la Comisi3n de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- 1.1. Descripci3n: Folios: 43 a 70
- 1.2. Reivindicaciones: Folios: 71 a 74 capitulo reivindicatorio original.  
Folios: 168 capitulo reivindicatorio modificado.
- 1.3. Prioridad: Folios: 8 a 16 ( Reino Unido, 27 de marzo de 2001, No. 0107651.2)
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- 1.6 Respuesta del solicitante Folios: 162 a 165.

## 2. Análisis de la Prioridad

La materia contenida en la prioridad que reclama el solicitante es la misma materia de la invención que se reclama en la solicitud por lo tanto la prioridad es aceptada.

## 3. Objeto de la invención

- *Título de la solicitud: " Composición acuosa que comprende una sal de paraquat y alginato".*

El objeto de la presente solicitud de patente de invención consiste en:

Reivindicaciones 1a 7: Una composición acuosa que comprende una sal de paraquat en una cantidad desde 50 a 400 g/l de la composición y un alginato en una cantidad desde 3 a 50 g/l de la composición, comprendiendo además la composición un emético y un purgante de modo tal que el efecto inductor de gelificación por pH tiene lugar al pH del jugo gástrico humano. El alginato de la composición tiene una viscosidad en solución acuosa al 1% de 2 a 1000mPas. El contenido de calcio del alginato es menor al 1%. El pH de la composición se ajusta entre 4 y 9. El emético es el compuesto 2-amino-6-metil-5-oxo-4-n-propil-4,5-dihidro-(1,2,4)triazolo(1,5-a)-pirimidina. El purgante es sulfato de magnesio.

El solicitante presenta, en el capítulo descriptivo el siguiente objeto de la invención: " Esta invención se relaciona con una composición y, en particular, con una composición herbicida acuosa, especialmente una formulación acuosa de bipiridilo. La invención también se relaciona con el uso de un alginato como agente gelificante en tal formulación".

- *Clasificación Internacional de Patentes (IPC.): A01N 43/40*

## 4. Determinación del Estado de la Técnica

La fecha que se ha tenido en cuenta para determinar el Estado de la Técnica es la fecha de presentación de la solicitud prioritaria la cual corresponde al 27 de marzo del 2001. Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

| Nº | Documento     | Título                                           | Fecha de publicación |
|----|---------------|--------------------------------------------------|----------------------|
| D1 | EP 0467529 A2 | Herbicial Compositions                           | 1992-01-22           |
| D2 | WO 8702864    | Contrade-glutitious solid herbicidal composition | 1987-05-21           |

## 5. Análisis de patentabilidad (artículo 14 D486)

### 5.1. Nivel inventivo (artículo 18 D486)

En el documento D1 se esta presentando una composición herbicida que tiene una sal cuaternaria de bipiridilio como ingrediente activo. La composición comprende una sal de diquat o paraquat, o una mezcla de ellas, las cuales se encuentran mezcladas con un agente gelificante el cual puede gelificar al pH del jugo gástrico humano además comprende un emético, un purgativo o la combinación de ambos. Preferiblemente las composiciones tienen entre 50 a 100 g/l de paraquat, diquat o la mezcla de ambos. Si una cierta cantidad de la composición se ingiere, la acidez del jugo gástrico permite que esta se gelifique en el estómago, incrementando la viscosidad del contenido de los jugos gástricos e impidiendo que el intestino delgado absorba la composición. El emético presente en la composición se absorbe rápidamente y ocasiona la expulsión del gel por medio del vómito. En el caso eventual en el cual la composición sea ingerida los efectos combinados del agente gelificante, el emético y, cuando se incluye, del purgativo pueden reducir sustancialmente la absorción del compuesto de bipiridilo del tracto gastrointestinal hacia el flujo sanguíneo y de esta manera reducir la toxicidad oral de la solución concentrada. Las composiciones de la invención comprenden principalmente paraquat, trisilicato de magnesio como gelificante y sulfato de magnesio como purgativo.

En el documento D2 se esta presentando una composición herbicida que contiene paraquat. Este principio activo es muy utilizado por su alto efecto herbicida y también por la facilidad de aplicación del mismo. Se han presentado varios casos de envenenamiento por composiciones herbicidas que contienen paraquat dado su alto grado de toxicidad. Se han realizado varios intentos para prevenir el envenenamiento o con paraquat, ya que a las composiciones que contienen este ingrediente activo se les adicionan sustancias nauseabundas par evitar la ingestión oral del mismo. Pero este mecanismo no es efectivo para niños y tampoco para ingesta intencional de los mismos, por lo que se han adicionando a la composición varios compuestos que permiten una remoción rápida del paraquat del estómago y otros órganos digestivos antes de su absorción en el organismo ya que una vez el paraquat se ingiere no existe un tratamiento que sea efectivo. La composición contiene alrededor de un 5% a 40% en peso, en cuanto a agentes gelificantes estos pueden ser de diversos orígenes típicamente se utilizan sales del ácido alginico, propilen glicol alginatos, goma de guar, entre otros. La adición de sales inorgánicas en la presente composición herbicida pueden impartir propiedades de gelificación a la presente composición herbicida. En lo ejemplos que se presentan en la anterioridad se tienen como componentes principales sales de paraquat, agente gelificante, carbón y surfactantes.

Como se puede observar, en la anterioridad las composiciones que contienen una sal de paraquat, con un componente gelificante y un emético y purgativo son presentadas por la anterioridad D1, mientras que composiciones de sal de paraquat con un agente gelificante que pude ser un alginato se encuentra presente en la anterioridad D2; por lo tanto, para una persona versada en la materia es fácilmente deducible la preparación de una composición que contenga: sal de paraquat, alginato, emético y purgativo. Escoger cada uno de los compuestos específicamente como el alginato como gelificante o el sulfato de magnesio como purgativo, se infiere por las características conocidas de dichos componentes así como lo descrito en las anterioridades.

De otra parte, tanto en las anterioridades como en la solicitud, este tipo de composiciones pretenden tener componentes que impidan la absorción del paraquat por el organismo en caso de una ingestión de esta solución de una forma voluntaria o involuntaria .

Por lo tanto, la solicitud no se encuentra presentando nivel Inventivo ya que se puede deducir según lo descrito en cada una de las anterioridades presentadas.

**13. Conclusión:**

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

| Nº | Documento Nº  | Reivindicaciones afectadas | Requisito que afecta |
|----|---------------|----------------------------|----------------------|
| D1 | EP 0467529 A2 | 1 a 7                      | NIVEL INVENTIVO      |
| D2 | WO 8702864    | 1 a 7                      | NIVEL INVENTIVO      |

**14 Respuesta a los argumentos del solicitante:**

El solicitante en su memorial de respuesta, detalla cada una de las modificaciones realizadas al capítulo reivindicatorio según las observaciones con respecto a claridad y concisión de las reivindicaciones presentadas en el capítulo reivindicatorio original; dando cumplimiento a cada una de las observaciones por lo que se aceptó el mencionado capítulo reivindicatorio y se procedió a realizar el estudio de patentabilidad presentando los documentos publicados en el estado del arte que afectan por Nivel Inventivo la solicitud y cuya argumentación al respecto se presentó en el numeral 12.1 del presente concepto.

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 Nº 10 de 2001.

**ALIX CARMENZA CÉSPEDES DE VERGEL**  
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 28 Dic. 2031

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| <b>CONCEPTO TÉCNICO No.</b><br>2623 | <b>EXAMINADOR TÉCNICO</b><br>Código No.202064 |
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