611593

FORM 1

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We, RHONE-POULENC CHIMIE, a French Company, of 25, Quai Paul Doumer, 92408, Courbevoie, France, hereby apply for the grant of a Standard Patent for an invention entitled:-

"GRANULES FOR SPREADING AND PROCESS FOR THEIR PREPARATION"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 88/12475

Country: France

Date: 23rd September, 1988

Our address for service is: SHELSTON WATERS
55 Clarence Street
SYDNEY, N.S.W. 2000.

DATED this 22nd Day of September, 1989
RHONE-POULENC CHIMIE

by

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

To: The Commissioner of Patents
WODEN A.C.T. 2606

File: D.B. R-45

Fee: $220.00

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CONVENTION APPLICATION BY A COMPANY

R 3905

FORM 8 - REGULATION 12 (2)

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by

(a) Here Insert (In full) Name of Company.

(a) RHONE-POULENC CHIMIE

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) Here Insert Title of Invention.

(b) "GRANULES FOR SPREADING AND PROCESS FOR THEIR PREPARATION"

(c) and (d) Here Insert Full Name and Address of Company Official authorised to make declaration.

I, (c) Madeleine-France FABRE

of (d) RHONE-POULENC, 25 quai Paul Doumer 92408 COURBEVOIE, FRANCE

do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

2. The basic Application(s) as defined by section 141 of the Act was / ~~were~~ made

(e) Here insert Basic Country followed by date of Basic Application.

(f) Here Insert Full Name(s) of Applicant(s) in Basic Country.

in (e) FRANCE on the 23rd day of September, 19 88

by (f) RHONE-POULENC CHIMIE

in ..... on the ..... day of 19

by .....

in ..... on the ..... day of 19

by .....

in ..... on the ..... day of 19

by .....

(g) Here insert (in full) Name and Address of actual Inventor or inventors.

3. (g) CHRISTIAN SEGAUD, of 33, rue Jean de la Fontaine - 69280 - CHASSIEU, FRANCE

..... is/~~are~~

the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the Application are as follows:

See reverse side of this form for guidance in completing this part.

Applicant is the assignee of the said inventor.

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/~~were~~ the first Application(s) made in a Convention country in respect of the invention, the subject of the Application.

DECLARED at COURBEVOIE, FRANCE

this 24 day of OCTOBER 19 89

(h) Personal Signature of Declarant (c) (no seal, witness or legalisation).

A-F Fabre

(h) Madeleine-France FABRE

(Signature of Declarant)

To THE COMMISSIONER OF PATENTS.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-41687/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 611593

(54) Title
GRANULES FOR SPREADING AND PROCESS FOR THEIR PREPARATION

International Patent Classification(s)
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A01N 025/14

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(71) Applicant(s)

RHONE-POULENC CHIMIE

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(57) The water-dispersible sulphonated polyesters which may form the binder are known products. They can be prepared by cocondensation of an organic diacid (such as a saturated or unsaturated aliphatic diacid, an aromatic diacid, a diacid containing several aromatic nuclei, or an arylaliphatic diacid), one of its diesters or its anhydride, with a sulphonated organic diacid or one of its diesters with a diol, in the presence of a conventional polyesterification catalyst such as tetraisopropyl orthotitanate.

As starting monomers commonly employed for the preparation of the water-dispersible sulphonated polyesters, there may be mentined, as:

- organic diacids: saturated or unsaturated aliphatic diacids, aromatic diacids, such as succinic, adipic,

.../2

suberic and sebacic acids, maleic, fumaric and itaconic acids, ortho-phthalic, isophthalic and terephthalic acids, anhydrides of these acids and their diesters, such as methyl, ethyl, propyl and butyl diesters. The preferred compounds are adipic acid and ortho-phthalic, isophthalic and terephthalic acids;

- sulphonated organic diacids: sodium sulphonate diacids or their diesters such as dialkyl isophthalates and dialkyl sulphosuccinates like sodium 5-dimethylisophthalatesulphonate or sodium dimethyl sulphosuccinate;

- diols: aliphatic glycols such as ethylene glycol, diethylene glycol, dipropylene glycol and the higher homologues, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and cyclanic glycols such as cyclohexanediol and dicyclohexanediolpropane. The diols which are preferably chosen are ethylene glycol and diethylene glycol.

The preferred water-dispersible sulphonated polyesters are those which have a number-average molecular mass of between 10,000 and 35,000, an acid value of less than 5 mg of KOH/g, and a sulphur content of between 0.8 and 2 % by weight, preferably between 1 2 and 1.8 %.

CLAIM

1. Granules for spreading based on at least one active ingredient for plant treatment and containing a binder, characterized in that the said binder comprises a water-dispersible sulphonated polyester.

7. Granules for spreading, characterized in that they contain

- from 2 to 97 % of their weight of active ingredient for plant treatment
- from 0.3 to 40 % of their weight of water-dispersible sulphonated polyester binder
- from 0 to 95 % of their weight of a filler
- from 0 to 25 % of its weight of a dispersing agent with binding property.

611593

COMMONWEALTH OF AUSTRALIA

FORM 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

FOR OFFICE USE:

Class Int.Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name of Applicant: RHONE-POULENC CHIMIE

Address of Applicant: 25, Quai Paul Doumer, 92408, Courbevoie, France

Actual Inventor: Christian Segaud

Address for Service: SHELSTON WATERS, 55 Clarence Street, Sydney

Complete Specification for the Invention entitled:

"GRANULES FOR SPREADING AND PROCESS FOR THEIR PREPARATION"

The following statement is a full description of this invention, including the best method of performing it known to us:-

GRANULES FOR SPREADING AND PROCESS FOR THEIR PREPARATION

The present invention relates to granules for spreading, containing active ingredients for plant treatment and to a process for their preparation; a property of these granules is that they disintegrate and slowly release the active ingredient, and this enables soils to be treated in a uniform manner.

The granules for spreading, based on at least one active ingredient for plant treatment and forming the subject of the invention, contain a binder and are characterized in that the said binder comprises a water-dispersible sulphonated polyester.

Among the active ingredients for plant treatment forming part of the composition of the granules of the invention there may be mentioned insecticides, acaricides, fungicides and their various combinations, herbicides, nematocides, molluscicides, attractants, repellants and rodenticides.

As examples of insecticides there may be mentioned those belonging to the groups of:

- organohalogen or chlorine compounds,
- carbinols,
- organophosphorus compounds,
- sulphones and sulphonates,
- carbamates,
- benzoylureas,

- synthetic pyrethrinoids.

The fungicides may be chosen from:

- carbamates,
- benzene derivatives,
- phenol derivatives,
- quinones,
- dicarboximides,
- amines, amides,
- diazines,
- sulphamides and sulphur derivatives,
- guanidines,
- heterocyclic compounds,
- metal monoethyl phosphites,
- organostannic compounds.

By way of chemical substances exhibiting herbicidal properties, use may be made of those to be found in the following chemical classes:

- phenolic compounds,
- carbamates,
- substituted ureas,
- diazines,
- triazines,
- amides,
- quaternary ammonium compounds,
- benzonitriles,
- toluidines,
- triazoles and others.

The water-dispersible sulphonated polyesters which may form the binder are known products. They can be prepared by cocondensation of an organic diacid (such as a saturated or unsaturated aliphatic diacid, an aromatic diacid, a diacid containing several aromatic nuclei, or an arylaliphatic diacid), one of its diesters or its anhydride, with a sulphonated organic diacid or one of its diesters with a diol, in the presence of a conventional polyesterification catalyst such as tetraisopropyl orthotitanate.

As starting monomers commonly employed for the preparation of the water-dispersible sulphonated polyesters, there may be mentined, as:

- organic diacids: saturated or unsaturated aliphatic diacids, aromatic diacids, such as succinic, adipic, suberic and sebacic acids, maleic, fumaric and itaconic acids, ortho-phthalic, isophthalic and terephthalic acids, anhydrides of these acids and their diesters, such as methyl, ethyl, propyl and butyl diesters. The preferred compounds are adipic acid and ortho-phthalic, isophthalic and terephthalic acids;

- sulphonated organic diacids: sodium sulphonate diacids or their diesters such as dialkyl isophthalates and dialkyl sulphosuccinates like sodium 5-dimethylisophthalatesulphonate or sodium dimethyl sulphosuccinate;

- diols: aliphatic glycols such as ethylene glycol, diethylene glycol, dipropylene glycol and the higher

homologues, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and cyclanic glycols such as cyclohexanediol and dicyclohexanediolpropane. The diols which are preferably chosen are ethylene glycol and diethylene glycol.

The preferred water-dispersible sulphonated polyesters are those which have a number-average molecular mass of between 10,000 and 35,000, an acid value of less than 5 mg of KOH/g, and a sulphur content of between 0.8 and 2 % by weight, preferably between 1.2 and 1.8 %.

The present invention is aimed more particularly at granules for spreading containing:

- from 2 to 97 % of their weight, preferably from 5 to 95 % of their weight of active ingredient for plant treatment
- from 0.3 to 40 % of their weight, preferably from 1 to 15 % of their weight, very particularly from 5 to 15 % of their weight of water-dispersible sulphonated polyester binder
- from 0 to 95 % of their weight, preferably from 0 to 85 % of their weight of a filler
- from 0 to 25 % of their weight, preferably from 0 to 10 % of their weight of a dispersing agent with a binding property.

The fillers are inert compounds which can be used:

- either as a carrier for the active ingredient and the various constituents if they are liquid

- or as a dilution agent for the active ingredient.

These are ground natural substances such as kaolin, attapulgite, bentonite, chalk, talc, or synthetic products such as precipitated or pyrogenic silica, calcium carbonate, and the like.

Among the dispersants with a binding property there may be mentioned naphthalenesulphonates, condensed sodium methylnaphthalenesulphonates, condensed 4,4-dihydroxydiphenyl sulphones, and sodium or potassium salts of maleic anhydride-diisobutylene copolymers, optionally mixed with an ethoxylated distyrylphenol.

Besides these main constituents there may be present:

- nonionic, anionic or cationic surface-active agents; there may be mentioned:

as nonionic surface-active agents: ethoxylated fatty alcohols, ethoxylated alkylphenols, esters of fatty acids and of glycerol, esters of fatty acids and of polyethylene glycol, esters of sorbitan and of optionally ethoxylated fatty acids, ethoxylated oils and fats, optionally ethoxylated fatty acid mono- and diethanol-amides, oxyethylene/oxypropylene block copolymers, saccharoglycerides, etc,

as example of anionic surface-active agents: alkali metal or ammonium salts of fatty acids or of aminocarboxylic acids (N-acylsarcosinates), sulphonates and sulphonated derivatives such as alkylbenzene-

sulphonates, naphthalenesulphonates, lignosulphonates, alkanesulphonates, sulphonated olefins, dialkyl sulphosuccinates, amidosulphonates (N-acyl-N-alkyltaurates), 2-sulphoethyl esters of fatty acids (acyl isethionates), etc; sulphates and sulphated derivatives such as optionally ethoxylated sulphated fatty alcohols, sulphated ethoxylated alkylphenols, sulphated fatty acids, sulphated fatty acid esters, sulphated alkanolamides, sulphated natural oils and fats, etc, and phosphoric esters of ethoxylated alkylphenols or of ethoxylated fatty alcohols, etc,

as example of cationic surface-active agents: amine oxides, ethoxylated alkylamines, etc,

- other binders such as polyvinyl alcohol, polyacrylate salts, xanthan gum,

- antistatic agents which may be inorganic salts such as lithium chloride or organic phosphates such as phosphates of fatty alcohols or fatty acids, especially the potassium salt of tridecylphosphoric acid,

- protective agents enabling the active ingredient to be stabilized against oxidation, UV rays and pH variations (buffer mixture) and

- various other additives such as colorants, adjuvants, repellants and attractants.

The granules for spreading forming the subject of the invention are obtained by agglomeration of the active ingredient with the binder and the other constituents

which may be present.

The agglomeration operation may be carried out according to the conventional granulation processes, for example in a fluidized bed, by spraying if the melting temperature of the active ingredient permits, by extrusion, by granulation on a rotary tray, etc.

If the active ingredient is in the liquid state, it is quite possible to absorb it onto a pulverulent carrier, to have a solid formulation.

Precipitated silicas of high absorption capacity, used in sufficient quantity to obtain a dry powder, or else calcium silicates, are preferably chosen.

Various methods of preparing granules, illustrating the various granulation methods are given below, no limiting character being implied.

The preparation of the granules in a fluidized bed consists in making a premix of the solid active ingredient (ground or absorbed on a carrier) with whole or some of the quantity of binder and of any other constituents used, and then spraying onto this premix water optionally containing the fraction of binder which is not premixed.

The material is kept in a fluidized state by means of a rising stream of warm air from 20 to 80°C.

When the granules have been formed, they can be dried with the aid of a stream of warm air at a temperature below the melting or decomposition temperature of

the active ingredient.

The size of the granules obtained may vary within quite wide limits between 0.1 and 2 mm.

The spray-granulation method consists in spraying into a stream of hot air at between 140 and 240°C a concentrated slurry (50 to 70 % of solid content) containing water, the active ingredient, the binder and the other constituents which may be present.

The size of the granules obtained generally varies between 100 and 500 μm.

Another method of granulation consists in agglomerating the active ingredient on a rotary tray.

The solid materials (active ingredient, all or some of the binder and the other constituents which may be present) are charged onto the rotary tray and the mixture of the said materials is homogenized by rotating the tray.

To agglomerate the active ingredient, a water spray is applied, optionally additionally containing a proportion of binder and of surface-active agent in liquid form.

The granules thus obtained must be dried in a second stage to a water content of 0.3 to 1 %, depending on the active ingredient.

The drying operation is carried out at a temperature below the melting or decomposition temperature of the active ingredient. It may be performed in air or

under reduced pressure.

The granules are more or less spherical in shape and their size varies between 100 and 500 μm.

The extrusion granulation method takes place as follows:

In a first stage, a powder/powder mixing is carried out of the active ingredient, ground or on a carrier, of the binder in solid form and of the other constituents which may be present in solid form.

The mixture obtained is moistened by addition of 10 to 30 % by weight of water. The addition of water may be performed by spraying.

The mixing of the constituents is carried out in a powder mixer of known type.

The paste obtained is then extruded, generally in an equipment operating at low pressure.

After extrusion, the granules must be dried.

Their dimensions are of the order of 1 to 4 mm in length and 0.5 to 2 mm in diameter.

The granules for spreading forming the subject of the invention have the advantage of disintegrating and of slowly releasing the active ingredient.

This property allows them to be employed for treating soils in order to combat parasites, for crop protection, etc.

The following examples are given by way of guidance and cannot be considered as a limit of the scope

and of the spirit of the invention.

The granules for spreading were prepared in the following general manner:

The following are mixed:

- the active ingredient(s)
- optionally, the carrier consisting of Rhône-Poulenc silica Zeosil 39 AB
- the binder based on water-dispersible sulphonate polyester
- Argirec B24 kaolin marketed by Blancs Minéraux de Paris
- optionally a dispersing agent

in a Moritz-type rapid mixer marketed by Moritz.

Moistening is carried out by spraying with water.

The moist paste obtained is then extruded in an Alexander Werk AGM/R extruder fitted with rolls, marketed by Alexander Werk.

Granules 1 mm in diameter and 2.5 mm in length are thus obtained.

These are then dried in an oven at 50°C for 1 hour and are then screened at 200 microns in order to remove dust.

Disintegration control

The control of granule disintegration is carried out using an apparatus consisting of a glass column with a working height of 25 cm and an inner diameter of 15 mm provided with a glass sinter at its base and fitted:

- with a stopcock in its lower part

- with a pump connected to a distilled water reservoir, in its upper part; the output of this pump is set at 11 ml/minute.

A collecting receiver is situated under the column.

The following are introduced into the column:

2 g of glass beads with a diameter of between 0.5 and 0.75 mm

in successive layers, 0.2 g of granules to be tested and 8 g of glass beads

them 2 g of glass beads.

The column is filled with distilled water, slowly at first and then quickly up to a height of 15 cm above the packing.

The pump is started up and the lower stopcock is opened so as to keep the height of water in the column constant. This percolation is maintained at a rate of 11 ml/minute, the collector receiver being changed every 10 minutes.

The percolator is stopped when the last fraction collected is perfectly clear, corresponding to the disintegration of the granules.

The larger the number of fractions collected which are not clear, the slower the granule disintegration.

Example 1

Granules are prepared according to the method described above, from:

- 7.5 g of diazinon adsorbed on 5 g of Zeolex 39
- 6.5 g of dry Gerol PS 30 (water-dispersible sulphonated polyester marketed by Rhône-Poulenc)
- 80 g of kaolin
- 15 g of water.

The result of the disintegration test is shown in Table I.

Example 2

The operation described in Example 1 is repeated, the 6.5 g of Gerol PS 30 being replaced with 6.5 g of dry Gerol PS 20, another sulphonated polyester marketed by Rhône-Poulenc.

The result of the disintegration test is shown in Table I.

Examples 3 and 4

The operation described in Example 1 is repeated, the 6.5 g of Gerol PS 30 being replaced with:

- 6.5 g of Geropon HB, sodium polyacrylate with a mass in the region of 5000, marketed by Rhône-Poulenc (Example 3)
- 6.5 g of Geropon DG, potassium polymethacrylate with a mass in the region of 3000, marketed by Rhône-Poulenc (Example 4).

The results of the disintegration test are shown in Table I.

Example 5

Granules are prepared according to the method described above from:

- 7.5 g of diazinon adsorbed on 5 g of Zeolex 39
- 7.5 g of butocarboxim dissolved in 1.3 g of xylene and adsorbed onto 5.9 g of Zeolex 39
- 10 g of Gerol PS 30
- 62.8 g of kaolin
- 19 g of water.

The result of the disintegration test is shown in Table II.

Example 6

The operation of Example 5 is repeated, the 10 g of Gerol PS 30 being replaced with 10 g of Rhodoviol 30/70, polyvinyl alcohol marketed by Rhône-Poulenc.

The result of the disintegration test is shown in able II.

Example 7

Granules are prepared according to the method described above from:

- 80 g of preground lindane
- 5 g of Gerol PS 30
- 3 g of Supragil MNS 90, condensed sodium methyl-naphthalenesulphonate marketed by Rhône-Poulenc
- 12 g of kaolin

- 21 g of water.

The result of the disintegration test is shown in Table II.

The abbreviations shown in Tables I and II have the following meaning:

VC	:	very cloudy	VSC	:	very slightly cloudy
C	:	cloudy	VLC	:	very little cloudiness
MC	:	moderately cloudy	WC	:	water-clear
SC	:	slightly cloudy			

TABLE I

FRACTION	EXAMPLE			
	1	2	3	4
	APPEARANCE OF THE FRACTION			
1	C	MC	VC	VC
2	C	MC	C	C
3	MC	MC	WC	MC
4	SC	MC		SC
5	SC	MC		SC
6	SC	MC		WC
7	SC	VSC		
8	SC	VLC		
9	VSC	VLC		
10	VSC	VLC		
11	VSC	WC		
12	VSC			
13	WC			

TABLE II

FRACTION	EXAMPLE 5 APPEARANCE OF THE FRACTION	6	7
1	C	C	C
2	C	C	C
3	MC	SC	MC
4	SC	VSC	SC
5	SC	WC	SC
6	SC		SC
7	SC		VSC
8	SC		WC
9	VSC		
10	VSC		
11	VSC		
12	WC		

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Granules for spreading based on at least one active ingredient for plant treatment and containing a binder, characterized in that the said binder comprises a water-dispersible sulphonated polyester.

2. Granules according to Claim 1), characterized in that the water-dispersible polyester is obtained by co-condensation of:

1) an organic diacid or one of its diesters or its anhydride and,

2) a sulphonated organic diacid or one of its diesters with a diol,

in the presence of a polyesterification catalyst.

3. Granules according to Claim 2), characterized in that the organic diacid is a saturated or unsaturated aliphatic diacid, a diacid containing a number of aromatic nuclei or an arylaliphatic diacid.

4. Granules according to Claim 2 or 3, characterized in that the diester of sulphonated organic diacid is a sodium dialkyl isophthalate sulphonate or a sodium dialkyl sulphosuccinate.

5. Granules according to any one of Claims 2 to 4, characterized in that the diol is an aliphatic glycol or a cyclanic glycol.

6. Granules according to any one of the preceding claims, characterized in that the water-dispersible sulphonated polyester has a number-average molecular mass of between 10,000 and 35,000 an acid value of less than 5 mg of KOH/g and a sulphur content of between 0.8 and

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2 % by weight.

7. Granules for spreading, characterized in that they contain

- from 2 to 97 % of their weight of active ingredient for plant treatment
- from 0.3 to 40 % of their weight of water-dispersible sulphonated polyester binder
- from 0 to 95 % of their weight of a filler
- from 0 to 25 % of its weight of a dispersing agent with binding property.

8. Granules according to the preceding claim, characterized in that they contain:

- from 5 to 95 % of their weight of active ingredient for plant treatment
- from 1 to 15 % of their weight of water-dispersible sulphonated polyester binder
- from 0 to 85 % of their weight of a filler
- from 0 to 10 % of its weight of a dispersing agent with binding property.

9. Process for the preparation of granules for spreading forming the subject of any one of the preceding claims, by agglomeration of the active ingredient with the water-dispersible sulphonated polyester and the optional other constituents.

10. Granules in accordance with claim 1 substantially as herein described with reference to the examples.

11. Process in accordance with claim 9 substantially as herein before described with reference to the examples.

DATED this 22nd Day of September, 1989
RHONE-POULENC CHIMIE

Attorney: IAN ERNST
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS