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

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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__

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83**United States Patent** [19]**Bourgogne et al.**[11] **Patent Number:** **5,705,193**[45] **Date of Patent:** **Jan. 6, 1998**[54] **METHOD FOR PREPARING GRANULES
CONTAINING ONE OR MORE ACTIVE
PRINCIPLES**[75] **Inventors:** **Michel Bourgogne; Colette Meinard,**
both of Marseille, France[73] **Assignee:** **Roussel Uclaf, France**[21] **Appl. No.:** **666,549**[22] **PCT Filed:** **Dec. 21, 1994**[86] **PCT No.:** **PCT/FR94/01506**§ 371 Date: **Jun. 20, 1996**§ 102(e) Date: **Jun. 20, 1996**[87] **PCT Pub. No.:** **WO95/17089****PCT Pub. Date:** **Jun. 29, 1995**[30] **Foreign Application Priority Data**

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[51] **Int. Cl.⁶** **A61K 9/14**[52] **U.S. Cl.** **424/489; 424/405; 424/409;**
424/408; 424/470[58] **Field of Search** **424/409, 489,**
424/408, 405, 406, 455, 470; 260/465;
71/96[56] **References Cited****U.S. PATENT DOCUMENTS**4,261,921 4/1981 Smeltz 260/465
4,913,722 4/1990 Felix et al. 71/90**FOREIGN PATENT DOCUMENTS**9008467 8/1993 Australia .
0127773 12/1984 European Pat. Off. .
0213328 3/1987 European Pat. Off. .
2210884 6/1989 United Kingdom .
9314631 8/1993 WIPO .**Primary Examiner**—Thurman K. Page**Assistant Examiner**—William E. Benston, Jr.**Attorney, Agent, or Firm**—Bierman, Muscrlian & Lucas[57] **ABSTRACT**

A process for the preparation of granules containing at least one active principle with a melting point above 70° C. selected from the group consisting of herbicides, fungicides and insecticides comprising dissolving the active principle in an aromatic solvent or pyrrolidone, absorbing the resulting solution on a support, optionally adding water thereto and drying the resulting product to form the granules and the granules produced thereby which have a superior biological activity than a granule dispersible in water with good stability.

11 Claims, No Drawings

METHOD FOR PREPARING GRANULES CONTAINING ONE OR MORE ACTIVE PRINCIPLES

The present invention relates to a new process for preparing emulsions or suspo-emulsions, dry or extruded in the form of granules, and the granules thus obtained.

The presentation of the active material in the form of an emulsion allows granules to be obtained which are endowed with a biological activity superior to that of a granule dispersible in water obtained by drying of a concentrated suspension of an active principle.

The subject of the invention is a process for preparing granules containing one or more active principles characterized in that the said active principle or principles is or are dissolved in a solvent, a solution is obtained which is absorbed on a support (or a filler) which may contain another active principle, a product is obtained to which water is or is not added, and which is dried and given the form of granules.

The support or filler can be chosen from the group of the following products: clays, bentonites, lactoses, starches, silicas, silicates, sulphates, and chlorides of alkaline and alkaline-earth metals.

In a preferred embodiment, the quantity of support used is less than 60% (m/m) of the total quantity of the ingredients used.

Citable as solvent are aromatic hydrocarbons, such as 1-methylnaphthalene, tetrahydronaphthalene, decahydronaphthalene, 2-methylnaphthalene or dimethylnaphthalene, alkylbenzenes, xylene (including Solvesso 200®), mixtures of isomers of dibenzyltoluene such as Marlotherm S®, or mixtures of isomers of benzyltoluene such as Marlotherm L®, aliphatic hydrocarbons, mineral or vegetable oils, alcohols such as cyclohexanol, C8 alcohols, ethers such as dibenzylether, ketones such as cyclohexanone or 4-methylcyclohexanone, amides such as N,N-dimethylcaprylamide capramide (HALLCOMID® M 8-10), esters such as alkyl benzoates (ethyl, propyl, n-butyl for example), mono and dialkyl phthalates (of ethyl, of propyl or of n-butyl, for example), pyrrolidones such as N-methylpyrrolidone, N-octylpyrrolidone (AG SOL EX 8®), N-dodecylpyrrolidone (AG SOL EX 12®), N-cyclohexylpyrrolidone or mixtures of these solvents, such as Surfadone LP 100®. Also citable are TBP or tributyl phosphate, dibenzylether, N-butyl benzoate.

Citable as preferred solvent are aromatic solvents such as Solvesso 200®, or pyrrolidones such as Surfadone LP 100®.

In a preferred embodiment, the quantity of solvent used is between 20 and 40% (m/m) of the total quantity of the ingredients used.

The active principle can be of a very varied nature: it is preferably a pesticide.

The subject of the invention is in particular the process characterized in that the active principle is a herbicide, an insecticide or a fungicide.

The subject of the invention is more particularly the process characterized in that the active principle has a melting point above 70° C.

The subject of the invention is quite particularly a process which is characterized in that the active principle is a pyrethrinoid. The latter can be alone or associated with other active principles such as pyrimicarb or the derivatives of β -methoxy acrylic acid or the lipidamides.

Among the pyrethrinoids usable for the preparation of the granules of the invention can be cited deltamethrin, cypermethrin, alphamethrin, tralomethrin, cyalothrine,

fenvalerate, cyfluthrine, flucythrinate, fluvalinate, fenpropathrine, tefluthrine, bifenthrine, acrinathrine, esfenvalerate, betacyfluthrine, taufluvalinate or lambda-cyhalothrine.

Deltamethrin can be cited as preferred pyrethrinoid.

In a preferred embodiment, the quantity of active principle used is less than 20% of the total quantity of the ingredients used.

The subject of the invention is in particular a preparation process which is characterized in that one or more of the following ingredients is added to the solvent: emulsifiers and stabilizers.

The subject of the invention is also a process which is characterized in that one or more of the following elements is also added: dispersants, wetting agents, binders, colorants, anti-foaming agents and adjuvants facilitating extrusion or lubricants.

Citable as emulsifiers are anionic emulsifiers such as calcium dodecylbenzene sulphonate or the phosphoric esters or non-ionic emulsifiers such as copolymers of ethylene oxide and propylene oxide, ethoxylated castor oil or ethoxylated fatty alcohols.

Citable as stabilizers are anti-oxidants such as butylhydroxytoluene or acids such as citric acid or acetic acid.

The dispersing agent can be an ionic or non-ionic surfactant or a mixture of such surfactants.

Citable as compounds that can be used as dispersing agent are for example polymers of the arylsulphonate type, in particular the alkaline polynaphthalene sulphonates obtained by condensation of (alkyl) aryl sulphonate derivatives with formaldehyde, lignosulphonates (for example: sodium lignosulphonate and calcium lignosulphonate), the polyphenol sulphonates, the salts of polyacrylic acids, the salts of lignosulphonic acids (for example: the sodium salt of polymerized lignosulphonic acids of the Kraft type), the salts of sulphonic phenol acids or sulphonic naphthalenes, the phosphoric esters of alcohols or of polyethoxylated phenols, the esters of fatty acids and of polyols, derivatives with a sulphates, sulphonates and phosphates function of the preceding compounds.

The wetting agent can be an ionic or non-ionic surfactant or a mixture of such surfactants.

Citable as compounds that can be used as wetting agent are, for example, the salts of the alkyl sulphate type (for example: sodium lauryl sulphate (SIPON LCS 98®), the salts of the alkyl ether sulphate type (for example: sodium lauryl ether sulphate), the salts of the alkyl aryl sulphonate type, in particular the alkaline alkyl naphthalene sulphonates, the salts of polycarboxylic acids, the polycondensates of ethylene oxide on fatty alcohols or on fatty acids or on fatty amines, the substituted phenols, in particular the alkylphenols or arylphenols, the salts of esters of sulphosuccinic acids, the salts of α -olefins sulphonates, derivatives of taurine, in particular alkyltaurates (for example: oleyl methyltaurate).

Citable as an agent promoting extrusion or lubricant is magnesium stearate or talc.

Citable as binder are sugars, polyvinyl and polyalkyl pyrrolidones, carboxymethyl cellulose and xanthan gum.

Silicones can be used as anti-foaming agents.

The subject of the invention is quite particularly a process, characterized in that there are used:

less than 50% of active principle m/m

20 to 40% of solvent m/m

0 to 5% of emulsifier m/m

0 to 5% of stabilizer m/m

0 to 15% of dispersant m/m

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0 to 10% of wetting agent m/m
0 to 5% of binder m/m
0 to 1% of lubricant m/m.

The granules thus obtained are in themselves a subject of the present invention.

The granules obtained according to the invention are easy to prepare, easy to use and present a good stability as well as a good biological activity.

The granules obtained according to the invention can be used in the field:

of agriculture for the treatment of crops,
of animals,
of the environment.

Pesticide compositions intended for the treatment of crops can be obtained very easily, by dispersing the granules in water.

It is possible for example to spread 50 to 1000 g per hectare of compositions prepared in this way, i.e. a dose per hectare of between 5 and 100 g of pyrethrinoid for example.

The granules of the invention preferably have a granulometry between 1 and 10 mm, for example between 2 and 6 mm.

The following examples illustrate the invention.

A—Preparation of the Granules of the Invention

The active material is dissolved in a solvent possibly comprising other elements (emulsifier, stabilizer).

The solution obtained is absorbed on a support (also called filler) possibly containing other elements (dispersant, wetting agent, binder). This is moistened by adding water in order to obtain a paste which is forced through a die. Extrudates are thus obtained, which are dried and cut to the desired size.

Procedure:

- 1—Dissolution accompanied by magnetic stirring of the active material in the solvent with possibly emulsifiers and stabilizers.
- 2—Mixing of the solid ingredients (fillers), dispersants, wetting agents, binders and possibly other active materials, in a homogenizer for powders.
- 3—Spraying of the organic solution of active material onto the solid filler (this can also be carried out on silica and then mixing with other ingredients).
- 4—Possibly grinding or deglomeration of the obtained product.
- 5—Moistening of the obtained powder with 0 to 50 g of water per 100 g of powder, preferably 10 to 20 g.
- 6—Extrusion on a die with holes of 0.5 to 3 mm (preferably 1 mm).
- 7—Drying of the obtained extrudates on a fluidized-air bed at temperatures between 20° and 150° C. (preferably 50° to 60° C.). Drying can take place in a stove, at ambient temperature, or in a microwave oven.
- 8—Cutting to the desired dimension.

Granules were prepared according to the procedure described above using the following ingredients:

EXAMPLE 1

INGREDIENTS	% m/m
Deltamethrin ®	3.27
Calcium phenylsulphonate ®	1.07
Emulsogen EL 360 ®	1.61
Solvesso 200 ®	32.40

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INGREDIENTS	% m/m
Wessalon S ®	20.65
Sipon LCS 98 ®	3.00
Geropon T 36 ®	7.00
Argirec B 24 ®	31.00

EXAMPLE 2

INGREDIENTS	% m/m
Deltamethrin ®	5.13
Soprofor PA 17 ®	3.48
Genapol PF 10 ®	0.38
Surfadone LP 100 ®	28.61
Wessalon S ®	20.00
Sipon LCS 98 ®	3.00
Geropon T 36 ®	5.00
BHT	0.04
Citric acid	0.004
Weegum F ®	3.00
Maize starch	31.36

EXAMPLE 3

INGREDIENTS	% m/m
Deltamethrin ®	5.13
Soprofor PA 17 ®	3.48
Genapol PF 10 ®	0.38
Surfadone LP 100 ®	28.61
Wessalon S ®	20.00
Sipon LCS 98 ®	3.00
Geropon T 36 ®	5.00
BHT	0.04
Citric acid	0.004
Sodium sulphate	3.00
Maize starch	29.36
Borresperce NA ®	2.00

Deltamethrin
solvent
dispersant

Dispersant
acid
Inerte

EXAMPLE 4

INGREDIENTS	% m/m
Deltamethrin ®	5.13
Soprofor PA 17 ®	3.48
Genapol PF 10 ®	0.38
Surfadone LP 100 ®	28.61
Wessalon S ®	25.64
Sipon LCS 98 ®	5.00
Geropon T 36 ®	10.00
BHT	0.04
Citric acid	0.004
Sodium sulphate	10.90
Sugar	10.00

EXAMPLE 5

INGREDIENTS	% m/m
Deltamethrin ®	5.13
Soprofor PA 17 ®	3.48
Genapol PF 10 ®	0.38
Surfadone LP 100 ®	28.61
Wessalon S ®	25.64
Sellogen DFL ®	5.00

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(54) COMPOSITION TERMICIDE SYNERGIQUE A BASE DE PYRETHROIDE ET DE N-PHENYL-PYRAZOLE

(54) SYNERGISTIC TERMITICIDAL COMPOSITION OF PYRETHROID AND N-PHENYL-PYRAZOLE

(57)

A termite control composition for soil treatment containing 3-cyano-1-(substituted phenyl) pyrazole derivative and a pyrethroid compound as effective ingredients, and a method of controlling pests such as termites using said composition. The termite control composition is improved for soil treatment as well as for the ability to prevent termites from passing through the pesticidally treated layer.

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materials, furniture, leather, fabrics, vinyl coated articles, electric wires, or cables.

- For the efficient use of the termite control composition for material or soil treatment of the present invention, the composition may be dissolved, suspended, mixed, adsorbed, or adhered on an appropriate solid and/or liquid vehicles (this word is used as a synonym of "carrier") according to the formulation generally used, together with auxiliary agents if required. This composition may be formulated into forms suited to the object of use, for example, an oil solution, emulsion, water solution, powder, granules, wettable powder, aerosol, smoking agent, or flowable agent.

- Solid vehicles used in the present invention include, for example, clays such as kaolin, bentonite, and acid clay; talc materials such as talc and pyrophyllite; siliceous materials such as diatomaceous earth, silica sand, mica, synthetic silicates, and high dispersion synthetic silicates; and inorganic mineral powders such as pumice and sand. Liquid vehicles include, for example, alcohols such as methanol, ethanol, and ethylene glycol; ketones such as acetone, methylethyl ketone, and cyclohexanone; ethers such as ethyl ether, dioxane, tetrahydrofuran, and cellosolve; aliphatic hydrocarbons such as kerosene; aromatic hydrocarbons such as benzene, toluene, xylene, solvent naphtha, cyclohexane, and methyl naphthalene; and halogenated hydrocarbons such as chloroform, carbon tetrachloride, and chlorobenzene. These solid or liquid vehicles may be used alone or in combination.

- Auxiliary agents used in the present invention include propellants, surface-active agents, fixing agents, dispersing agents, thickening agents, and bonding agents. Propellants include, for example, liquefied petroleum gas, dimethyl ether, and fluorocarbons. Surface-active agents include, for example, polyoxyethylene alkylaryl ether, polyoxyethylene sorbitane monolaurate, alkylaryl sorbitane monolaurate, alkylbenzene sulfonate, alkyl naphthalene sulfonate, lignin sulfonate, and sulfuric acid ester salts of higher alcohols. These surface-active agents may be used alone or in combination.

Fixing agents, dispersing agents, thickening agents, and bonding agents include, for example, casein, gelatine, starch, carboxymethyl cellulose, alginic acid, agar, polyvinyl alcohol, polyethylene glycol, polysodium acrylate, gum arabic, and xanthane gum, which may be used if required.

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The termite control composition for soil treatment of the present invention may contain co-operating agents such as sinepyrin 500, piperonyl butoxide, and S-421.

5 The termite control composition of the present invention may be used not only for treating the surface or the interior of surrounding soil or under-floor soil for protecting wood such as trees, fences, and railroad ties, or buildings such as houses, warehouses, and industrial plants, but also in timber products such as plywood and furniture, wood products such as particle boards and half boards, and vinyl products such as coated wires and sheets.

10 The present invention also includes the aspects for preventive uses in places where the breeding of termites is expected as well as the above aspects.

Emulsifying agents which may be used are one or more of those selected from non-ionic or anionic emulsifying agents. Examples of non-ionic emulsifying agents which may be mentioned include

15 polyoxyethylenealkylphenylether, polyoxyethylenealkylether, polyethyleneglycol fatty ester, sorbitan fatty ester, polyoxyethylene sorbitan fatty ester, polyoxyethylenesorbitol fatty ester, polyoxyethylenepolyoxypropylenealkylether. Examples of anionic emulsifying agents which may be mentioned include alkyl sulphates, polyoxyethylenealkylether sulphates, 20 sulfosuccinates, taurine derivatives, sarcosine derivatives, phosphoric esters, alkylbenzenesulfonates and the like. A mixture consisting of polyoxyethylenestyrylphenylether and calcium alkylbenzenesulfonate is preferred. These emulsifying agents may be used in an amount of 5 to 20 weight parts per 100 weight parts of the composition of the present invention.

25 Compositions of the present invention may be prepared by any of conventional procedures suitable for emulsifiable concentrates.

The present invention is illustrated by the following examples, comparative examples and experimental examples, but is not limited to the details thereof.

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EXAMPLES

Typical embodiments and test examples of the present invention will be shown below, but the present invention is not limited to these embodiments.

8) A composition according to any one of claims 1 to 7 wherein the pyrethroid compound is other than cyfluthrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate, and permethrin.

9) A composition according to any one of claims 1 to 7 wherein the pyrethroid compound is selected from a group consisting of allethrin, ethofenprox, cycloprothrin, cyhalothrin, cyfluthrin, cypermethrin, pyrethrin, tralomethrin, fenvalerate, fenpropathrin, flucythrinate, permethrin, bifenthrin, silafluofen, lesmethrin, tefluthrin, acrinathrin, prarethrin, cismethrin d-phenothrin, deltamethrin, and tetramethrin.

10) A method for controlling and preventing termites from passing through a pesticidally treated layer of soil or material whereby the said layer is treated by means of an effective amount of a composition according to any one of claims 1 to 9.

11) A method for controlling termites by soil treatment using 0.1 g/m² to 5 g/m² of a composition according to any one of claims 1 to 9.

12) A method for controlling pests of animals wherein the animal is treated by means of a composition according to any one of claims 1 to 9, the rate of application being between 0.1 and 100 mg per kilo of body weight of the animal.

13) The method according to claim 12, wherein the rate of application is between 2 and 20 mg per kilo of body weight of the animal.