

Singapore

PATENT SPECIFICATION

(11)

1281653

1281653

NO DRAWINGS

- (21) Application No. 5528/70 (22) Filed 5 Feb. 1970
(31) Convention Application No. P 19 05 524.4
(32) Filed 5 Feb. 1969 in
(33) Germany (DT)
(45) Complete Specification published 12 July 1972
(51) International Classification A01N 17/08
(52) Index at acceptance



A5E 1A1G3 1A2A 1A2B 1A2C 1A2F 1A2M 1A2N2
1A2N4 1A2X 1A3B 1A3C 1A3F 1A5A1 1A5B2
1A5B3 1C12H 1C15A7 1C15B2 1C15B3 1C15C2
1C15D3 1C4A 1C5J 1C5P 1C7D 1C7N 1C8A

(54) MICRO GRANULES CONTAINING PESTICIDES AND PROCESS FOR THEIR MANUFACTURE

(71) We, FARBWERKE HOECHST AKTIEN-
GESELLSCHAFT, vormals Meister Lucius &
Büning, a Body Corporate recognised under
German Law, of 6230 Frankfurt (M)-Hoechst,
Germany, do hereby declare the invention,
for which we pray that a patent may be
granted to us, and the method by which it
is to be performed, to be particularly des-
cribed in and by the following statement:

The present invention relates to micro size
granules for use in plant protection and to a
process for their manufacture.

In order also to rationalize the use of plant
protecting agents there is a demand for bring-
ing out products of a higher concentration than
has been hitherto usual. This means a distri-
bution of smaller volumes of formulated
pesticides per unit of cultivated area. Conven-
tional granules for pesticidal purposes have
a particle size of about 0.5 to 1.5 mm.

This invention provides micro granules con-
taining pesticides having a granular particle
size of from 0.075 to 0.4 mm which com-
prise a homogeneous content of a solid pesti-
cidal active ingredient having a particle size
of from 0.001 to 0.01 mm, together with an
adhesive, and, optionally, together with an
inert substance, a wetting agent, dispersing
agent and a protective colloid.

The present invention especially provides
micro granules containing pesticides, which
comprise the solid pesticidal active ingredient
in an amount of from 2 to 80 parts by weight,
from 10 to 80 parts by weight of an inert
substance, from 0 to 2 parts by weight of a
wetting agent, from 1 to 25 parts by weight
of a dispersion agent and from 0.5 to 10
parts by weight of the adhesive.

The present invention also provides a pro-
cess for the manufacture of micro granules
containing pesticides of a granular size of from
0.075 to 0.4 mm, which comprises grinding
a pesticide in the wet state together with an
adhesive, and optionally together with an
inert substance, wetting agent, dispersing

agent, and protective colloids in a ball mill
to yield a particle size of at most of 0.01
mm, preferably of 0.005 mm, and spray-drying
the suspension or paste thus obtained by means
of rotating discs at a circumferential speed of
from 80 to 100 m/sec., using single feed
nozzles under a spraying pressure of from 5
to 8 atmospheres gauge, or double feed nozzles
under a spraying pressure of from 0.5 to 4
atmospheres gauge, preferably from 0.5 to
1.5 atmospheres gauge, at a drying gas inlet
temperature of from 300 to 140°C, preferably
from 270 to 180°C, and at a drying gas
outlet temperature of from 50 to 120°C, pre-
ferably from 60 to 80°C.

The present invention also provides a pro-
cess as described above where within the range
of from 40 to 70 parts by weight of the dry
material is ground in 30 to 60 parts by weight
of water.

The present invention further provides a
process as described above wherein the finest
particles of the granules having a size below
0.075 mm are once more ground in an aqueous
medium and spray-dried.

The active ingredient particles in the micro
granules have a size of from 0.001 to 0.010
mm, advantageously of not more than 0.005
mm.

Owing to the above-mentioned small size
of the granules and hence a better distribu-
tion density to be achieved per unit of area,
the active ingredient concentration in the
granules can be increased to a content of 80%
by weight, preferably of from 2 to 20% by
weight, depending on the form of the pro-
duct and on the intended use. Alternatively,
compared with conventional granules, the
granules of the invention having the same con-
centrations of active ingredient permit a better
distribution effect which can still be increased
by the fine size and homogeneity of the active
ingredient particles within the separate
granules. In comparison to known sprays and
spraying liquors, the granules of the invention

[Price 25p]

SPECIFICATION AMENDED - SEE ATTACHED SLIP

can be used more accurately owing to their weaker tendency to wind drift which avoids damage to neighbouring cultures, as may especially result from the use of herbicides. Moreover, it is possible, as also in the case of coarse particles, to bring out the granules accurately, for example, in flooded rice cultures. The novel granules may also be spread out with the seeds by the drill or band method.

The process of the invention allows granulation of all solid pesticidal active ingredients, for example, herbicidal, insecticidal and fungicidal compositions, together with the inert material to be advantageously used for maintaining their chemical stability and their biological activity, for example, diatomaceous earth, silicic acids, kaolite-containing quartz, alumina, chalk, bentonites, attapulgite, inorganic salts, milk powder or starch.

The addition of a dispersing and/or wetting agent, for example, sodium or ammonium salt of lignin-sulphonic acid, sodium salt of dinaphthylmethane - disulphonic acid, sodium salt of butyl - naphthalene - sulphonic acid, oleylmethyl tauride sodium, sodium salt of an alkylphenyl - sulphonic acid, or condensation products of fatty acids and albumin permits a uniform distribution, wetting and release of the active ingredient particles. Depending on the type and dosage of the adhesive advantageously sodium salt of lignin-sulphonic acid, polyvinyl acetate, polyvinyl acetate copolymers and partially hydrolyzed polyvinyl alcohols or carboxymethyl cellulose having various polymerization degrees, vegetable rubber or glues, the release of the active ingredient can be accelerated or delayed.

It is not possible to prepare granules of the disclosed fine size according to known methods, for example, by adhesion of active ingredients to inert substance granules or by means of granulating cylinders. Neither can the granules of the desired particle size be obtained with a reasonable yield by subsequent grinding of coarse granules of known constitution.

According to the process of the invention, it is advantageous first to grind active ingredient concentrates in wet state in an aqueous suspension by means of friction ball mills to obtain a particle size of a maximum of 0.01 mm. The ground material is then stirred together with the above-cited additives in water into suspension or pastes having a dry material content of from 40 to 70% by weight. By incorporating a large amount of sodium or ammonium salt of lignin-sulphonic acid these can be maintained in a freely flowing state.

The process of the invention yields micro granules in an amount of from 80 to 90% and a particle size of from 0.075 to 0.4 mm.

The granules are separated by means of cyclones. The portions of from 10 to 20% of finest particles may be separated and granulated once more.

The granules of the invention have good flow properties.

The following Examples illustrate the invention, the parts and percentages being by weight unless otherwise stated.

EXAMPLE 1

Micro granules of pentachloronitro - benzene having an active ingredient content of 80%

(a) A mixture of 40 parts of pentachloronitro - benzene, 9 parts of sodium salt of lignin - sulphonic acid, 1 part of partially hydrolyzed polyvinyl acetate and 50 parts of water was ground in wet state in a friction ball mill to yield a grain size of from 1 to 5 microns; the paste or suspension thus obtained was then spray-dried in a drying tower by means of a single feed nozzle at a pressure of from 7 to 8 atmospheres gauge at an air inlet temperature of 240°C and an air outlet temperature of 75°C. 82 to 85% of the finest particles obtained had a size of from 0.075 to 0.350 mm. The content of active ingredient was 80%.

(b) Micro granules obtained according to the above method were mixed with 0.4 parts of a polyvinyl - acetate copolymer to slow down the release of the active ingredient.

EXAMPLE 2

Micro granules of pentachloronitro - benzene having an active ingredient content of 50%

A paste or suspension obtained according to Example 1 was stirred with further 1 part of partially hydrolyzed polyvinyl - acetate or 1 part of carboxymethyl cellulose, 5 parts of sodium salt of lignin - sulphonic acid, 24 parts of kaolinite-containing quartz powder or alumina and 5 parts of water and the mixture was spray-dried as disclosed above. The micro granules obtained had a size of from 0.075 to 0.4 mm and an active ingredient content of 50%.

EXAMPLE 3

Microgranules of pentachloronitro - benzene having an active ingredient content of 10%

A paste or suspension obtained according to Example 1 was stirred with further 5 parts of sodium salt of dinaphthyl - methane - di - sulphonic acid, 50 parts of sodium salt of lignin - sulphonic acid, 20 parts of sodium sulphate, 4 parts of carboxymethyl cellulose, 271 parts of bentonite or kieselguhr and 280 parts of water; this suspension having a solids content of 55% was spray-dried by means of a double feed nozzle at a spraying pressure of from 0.5 to 6.0 atmosphere gauge at a drying air inlet temperature of 250°C and a drying air outlet temperature of 75°C.

85% of the granules obtained had a size of from 0.075 to 0.4 mm and an active ingredient content of 10%.

EXAMPLE 4

Micro granules of linuron having an active ingredient content of 10%

- 5 In a manner analogous to Example 1, a paste or suspension containing 40% of linuron was prepared. This was stirred with further 35 parts of sodium salt of lignin - sulphonic acid, 3.5 parts of partially hydrolyzed poly - vinylacetate, 311.5 parts of kaolinite-containing quartz powder (or a mixture of 187 parts of keiselguhr and 124.5 parts of sodium hyperphosphate) and 215 parts of water in a colloidal mill. The suspension thus obtained having a solids content of 60% was spray-dried. 15 The yield of micro granules having a particle size of from 0.75 to 0.35 was 85%. The active ingredient content was 10%.

- 20 By adding from 0.1 to 1.5 parts of polyvinyl acetate in dispersed form the granules obtained had a slower release of active ingredient.

EXAMPLE 5

Micro granules of monolinuron having an active ingredient content of 10%

- 25 The suspension was prepared in a manner analogous to Example 4 using monolinuron instead of linuron.

EXAMPLE 6

- 30 Micro granules of monolinuron having an active ingredient content of 20%

- A paste of suspension obtained by grinding in wet state a mixture of 20 parts of monolinuron, 10 parts of partially hydrolyzed polyvinyl acetate, 15 parts of sodium salt of lignin - sulphonic acid, 20 parts of keiselguhr, 35 parts of sodium hyperphosphate and 70 parts of water was spray-dried by means of a single feed nozzle at a pressure of from 7 to 8 atmospheres gauge and at an air inlet temperature of 260°C an an air outlet temperature of 70°C. The yield of finest particles having a size of from 0.075 to 0.4 mm was 87% and the active ingredient content was 20%.

EXAMPLE 7

- 45 Micro granules of diuron having an active ingredient content of 10%

- The suspension was prepared in a manner analogous to Example 4 using diuron instead of linuron.

EXAMPLE 8

Micro granules of endosulfan having an active ingredient content of 20%

- 55 A paste or suspension obtained by grinding in wet state a mixture of 20 parts of endosulfan, 15 parts of sodium salt of lignin - sulphonic acid, 2 parts of sodium salt of dibutyl-naphthyl - sulphonic acid, 0.1 part of sodium salt of dodecyl - benzene - sulphonic acid, 0.5 part of partially hydrolyzed polyvinyl acetate, 10 parts of sodium sulphate, 52.4

parts of keiselguhr (pH of 7.5) and 70 parts of water the solids content being 59%, was spray-dried by means of a double feed nozzle under a pressure of 0.7 atmosphere gauge at a drying air inlet temperature of 250°C and a drying air outlet temperature of 70°C. The yield of micro granules having a size of from 0.075 to 0.35 mm was 88%. The active ingredient content was 20%.

EXAMPLE 9

Micro granules of triphenyl tin acetate having an active ingredient content of 20%

- (a) In a manner analogous to Example 8, but at a nitrogen inlet temperature of 240°C and a nitrogen outlet temperature of 70°C, a paste or suspension obtained by grinding in wet state a mixture of 20 parts of triphenyl - tin acetate, 15 parts of sodium salt of lignin-sulphonic acid, 0.5 parts of sodium salt of dodecyl - benzene - sulphonic acid, 21 parts of chalk, 10.5 parts of kaolite-containing quartz, 20 parts of sodium hyperphosphate, 3 parts of partially hydrolyzed polyvinyl acetate, 10 parts of milk powder and 70 parts of water was spray-dried by means of a double feed nozzle. The yield of micro granules having a particle size of from 0.1 to 0.4 mm was 82%.

- (b) In a manner analogous to (a), a paste or suspension of the following constitution: 20 parts of triphenyl tin chloride, 20 parts of sodium salt of lignin - sulphonic acid, 0.5 parts of sodium salt of dodecyl - benzene - sulphonic acid, 4 parts of partially hydrolyzed polyvinyl acetate or carboxymethyl cellulose, 25 parts of milk powder, 15 parts of sodium hyperphosphate, 15.5 parts of chalk or magnesium carbonate and 70 parts of water was spray-dried. The yield of micro granules having a particle size of from 0.1 to 0.4 mm was 80% and the active ingredient content was 20%.

WHAT WE CLAIM IS:—

1. Micro granules containing pesticides having a granular particle size of from 0.075 to 0.4 mm and comprising a homogeneous content of a solid pesticidal active ingredient having a particle size of from 0.001 to 0.01 mm together with an adhesive, and, optionally, together with in inert substance, a wetting agent, dispersing agent and protective colloid and being substantially free from water.
2. Micro granules as claimed in claim 1, the pesticidal active ingredient having a particle size of not more than 0.005 mm.
3. Micro granules containing pesticides as claimed in claim 1 or 2, which comprise the solid pesticidal active ingredient in an amount of from 2 to 80 parts by weight, from 10 to 80 parts by weight of an inert substance, from 0 to 2 parts by weight of a wetting agent, from 1 to 25 parts by weight of a

EXAMPLE 4

Micro granules of linuron having an active ingredient content of 10%

- 5 In a manner analogous to Example 1, a paste or suspension containing 40% of linuron was prepared. This was stirred with further 35 parts of sodium salt of lignin - sulphonic acid, 3.5 parts of partially hydrolyzed poly - vinylacetate, 311.5 parts of kaolinite-containing quartz powder (or a mixture of 187 parts of keiselguhr and 124.5 parts of sodium hyperphosphate) and 215 parts of water in a colloidal mill. The suspension thus obtained having a solids content of 60% was spray-dried.
- 15 The yield of micro granules having a particle size of from 0.075 to 0.35 mm was 85%. The active ingredient content was 10%.

- 20 By adding from 0.1 to 1.5 parts of polyvinyl acetate in dispersed form the granules obtained had a slower release of active ingredient.

EXAMPLE 5

Micro granules of monolinuron having an active ingredient content of 10%

- 25 The suspension was prepared in a manner analogous to Example 4 using monolinuron instead of linuron.

EXAMPLE 6

- 30 Micro granules of monolinuron having an active ingredient content of 20%

- A paste of suspension obtained by grinding in wet state a mixture of 20 parts of monolinuron, 10 parts of partially hydrolyzed polyvinyl acetate, 15 parts of sodium salt of lignin - sulphonic acid, 20 parts of keiselguhr, 35 parts of sodium hyperphosphate and 70 parts of water was spray-dried by means of a single feed nozzle at a pressure of from 7 to 8 atmospheres gauge and at an air inlet temperature of 260°C and an air outlet temperature of 70°C. The yield of finest particles having a size of from 0.075 to 0.4 mm was 87% and the active ingredient content was 20%.

EXAMPLE 7

- 45 Micro granules of diuron having an active ingredient content of 10%

- 50 The suspension was prepared in a manner analogous to Example 4 using diuron instead of linuron.

EXAMPLE 8

Micro granules of endosulfan having an active ingredient content of 20%

- 55 A paste or suspension obtained by grinding in wet state a mixture of 20 parts of endosulfan, 15 parts of sodium salt of lignin - sulphonic acid, 2 parts of sodium salt of dibutyl-naphthyl - sulphonic acid, 0.1 part of sodium salt of dodecyl - benzene - sulphonic acid, 0.5 part of partially hydrolyzed polyvinyl acetate, 10 parts of sodium sulphate, 52.4

parts of keiselguhr (pH of 7.5) and 70 parts of water the solids content being 59%, was spray-dried by means of a double feed nozzle under a pressure of 0.7 atmosphere gauge at a drying air inlet temperature of 250°C and a drying air outlet temperature of 70°C. The yield of micro granules having a size of from 0.075 to 0.35 mm was 88%. The active ingredient content was 20%.

EXAMPLE 9

Micro granules of triphenyl tin acetate having an active ingredient content of 20%

- (a) In a manner analogous to Example 8, but at a nitrogen inlet temperature of 240°C and a nitrogen outlet temperature of 70°C, a paste or suspension obtained by grinding in wet state a mixture of 20 parts of triphenyl tin acetate, 15 parts of sodium salt of lignin-sulphonic acid, 0.5 parts of sodium salt of dodecyl - benzene - sulphonic acid, 21 parts of chalk, 10.5 parts of kaolinite-containing quartz, 20 parts of sodium hyperphosphate, 3 parts of partially hydrolyzed polyvinyl acetate, 10 parts of milk powder and 70 parts of water was spray-dried by means of a double feed nozzle. The yield of micro granules having a particle size of from 0.1 to 0.4 mm was 82%.

- (b) In a manner analogous to (a), a paste or suspension of the following constitution: 20 parts of triphenyl tin chloride, 20 parts of sodium salt of lignin - sulphonic acid, 0.5 parts of sodium salt of dodecyl - benzene - sulphonic acid, 4 parts of partially hydrolyzed polyvinyl acetate or carboxymethyl cellulose, 25 parts of milk powder, 15 parts of sodium hyperphosphate, 15.5 parts of chalk or magnesium carbonate and 70 parts of water was spray-dried. The yield of micro granules having a particle size of from 0.1 to 0.4 mm was 80% and the active ingredient content was 20%.

WHAT WE CLAIM IS:—

1. Micro granules containing pesticides having a granular particle size of from 0.075 to 0.4 mm and comprising a homogeneous content of a solid pesticidal active ingredient having a particle size of from 0.001 to 0.01 mm together with an adhesive, and, optionally, together with an inert substance, a wetting agent, dispersing agent and protective colloid and being substantially free from water.
2. Micro granules as claimed in claim 1, the pesticidal active ingredient having a particle size of not more than 0.005 mm.
3. Micro granules containing pesticides as claimed in claim 1 or 2, which comprise the solid pesticidal active ingredient in an amount of from 2 to 80 parts by weight, from 10 to 80 parts by weight of an inert substance, from 0 to 2 parts by weight of a wetting agent, from 1 to 25 parts by weight of a



dispersing agent and from 0.5 to 10 parts by weight of the adhesive.

4. Micro granules as claimed in claim 1 and substantially as described in any one of Examples 1 to 9 herein.

5. A process for the manufacture of micro granules containing pesticides according to claim 1, having a granular particle size of from 0.075 to 0.4 mm which comprises grinding a pesticide in the wet state together with an adhesive and, optionally, together with an inert substance, a wetting agent, dispersing agent, and protective colloid, in a ball mill to yield a particle size of at most 0.01 mm, and spray-drying the suspension or paste thus obtained by means of discs rotating at a circumferential speed of from 80 to 100 m/sec. using single-feed nozzles under a spraying pressure of from 5 to 8 atmospheres gauge, or double-feed nozzles under a spraying pressure of from 0.5 to 4 atmospheres gauge, at a drying gas inlet temperature of from 300° to 140°C and at drying gas outlet temperature of from 50° to 120°C.

- 25 6. A process as claimed in claim 5, wherein within the range of from 40 to 70 parts by weight of the dry material is ground in 30 to 60 parts by weight of water.

- 30 7. A process as claimed in claim 5 or 6, wherein the particle size yielded of the pesticidal active ingredient is 0.005 mm.

8. A process as claimed in any one of claims 5 to 7, wherein the double feed nozzles are under a spraying pressure of from 0.5 to 1.5 atmospheres gauge.

9. A process as claimed in any one of claims 5 to 8, wherein the inlet temperature of the drying gas is within the range of from 270° to 180°C.

10. A process as claimed in any one of claims 5 to 9, wherein the outlet temperature of the drying gas is within the range of from 60° to 80°.

11. A process as claimed in any one of claims 5 to 10, wherein the finest particles of the granules, having a size below 0.075 mm are once more ground in an aqueous suspension and spray-dried.

12. A process as claimed in claim 5, conducted substantially as described in any one of the Examples herein.

13. Micro granules whenever prepared by a process claimed in any one of claims 5 to 12.

ABBI & IMRAY,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *