US006875381B2

(12) **United States Patent**
Jadhav et al.

(10) **Patent No.: US 6,875,381 B2**
(45) **Date of Patent: Apr. 5, 2005**

(54) **PROCESS FOR PREPARATION OF CHEMICALLY STABLE, DRY-FLOW, LOW COMPACT, DUST FREE, SOLUBLE GRANULES OF PHOSPHOROAMIDOTHIOATES**

(75) Inventors: **Prakash Mahadeo Jadhav**, Mumbai (IN); **Rajju Devidas Shroff**, Mumbai (IN)

(73) Assignee: **United Phosphorus, Ltd.**, Mumbai (IN)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 367 days.

(21) Appl. No.: **10/126,965**

(22) Filed: **Apr. 22, 2002**

(65) **Prior Publication Data**

US 2003/0127761 A1 Jul. 10, 2003

Related U.S. Application Data

(60) Provisional application No. 60/340,272, filed on Dec. 18, 2001.

(51) **Int. Cl.**[7] **B29B 9/00**
(52) **U.S. Cl.** **264/37.29**; 264/140
(58) **Field of Search** 514/120, 137, 514/75; 424/710; 264/37.29, 140, 330

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,716,600	A	2/1973	Magee
3,845,172	A	10/1974	Magee
3,914,417	A	10/1975	Magee
4,218,444	A	8/1980	Koundakjian
4,544,553	A	10/1985	Smolanoff
5,075,058	A	12/1991	Chan
5,100,667	A	3/1992	Chan
5,298,501	A	3/1994	Cummings
5,352,674	A	10/1994	Cummings
5,369,100	A	11/1994	Cummings
5,443,764	A	8/1995	Lloyd
5,464,623	A	11/1995	Chan
5,488,043	A	1/1996	Yamada
5,622,658	A	4/1997	Lloyd
5,650,163	A	7/1997	Cannelongo
5,698,540	A	12/1997	Katayama
6,013,272	A	1/2000	Cummings
6,337,323	B2	1/2002	Cummings
6,387,388	B1	5/2002	Misselbrook
2001/0018063	A1	8/2001	Cummings
2002/0091106	A1	7/2002	Cummings
2002/0114821	A1	8/2002	Lescota

FOREIGN PATENT DOCUMENTS

EP	0304492 B1	12/1994
JP	58067603	4/1983
JP	6-92803	4/1994
JP	9-124406	5/1997
WO	WO 98/26656	6/1998

OTHER PUBLICATIONS

International Specialty Products, "Granules & Tablets," Agrimer Polymers & Copolymers, International Specialty Products.

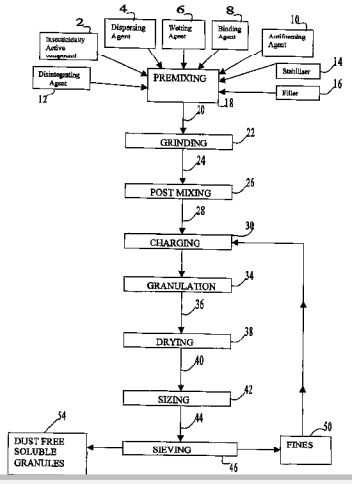
Fuji Paudal Co., Ltd., "Powder & Granulation Process Technology," Fuji Paudal Co., Ltd.

Primary Examiner—Mark Eashoo
(74) *Attorney, Agent, or Firm*—Jones, Tullar & Cooper, PC

(57) **ABSTRACT**

Dry flow, low compact, dust free, soluble granules of phosphoroamidothioates, preferably acephate, are produced by the process of 1) pre-mixing technical grade phosphoroamidothioate with specified adjuvants and other inert ingredients; 2) grinding to produce a ground product having a preferred particle size of 5 microns to 10 microns; 3) post-mixing; 4) granulating; 5) drying; 6) sizing to required length, preferably 1.5 to 3.0 mm; 7) and sieving to remove the fines to get the desired dust free soluble granule.

68 Claims, 1 Drawing Sheet



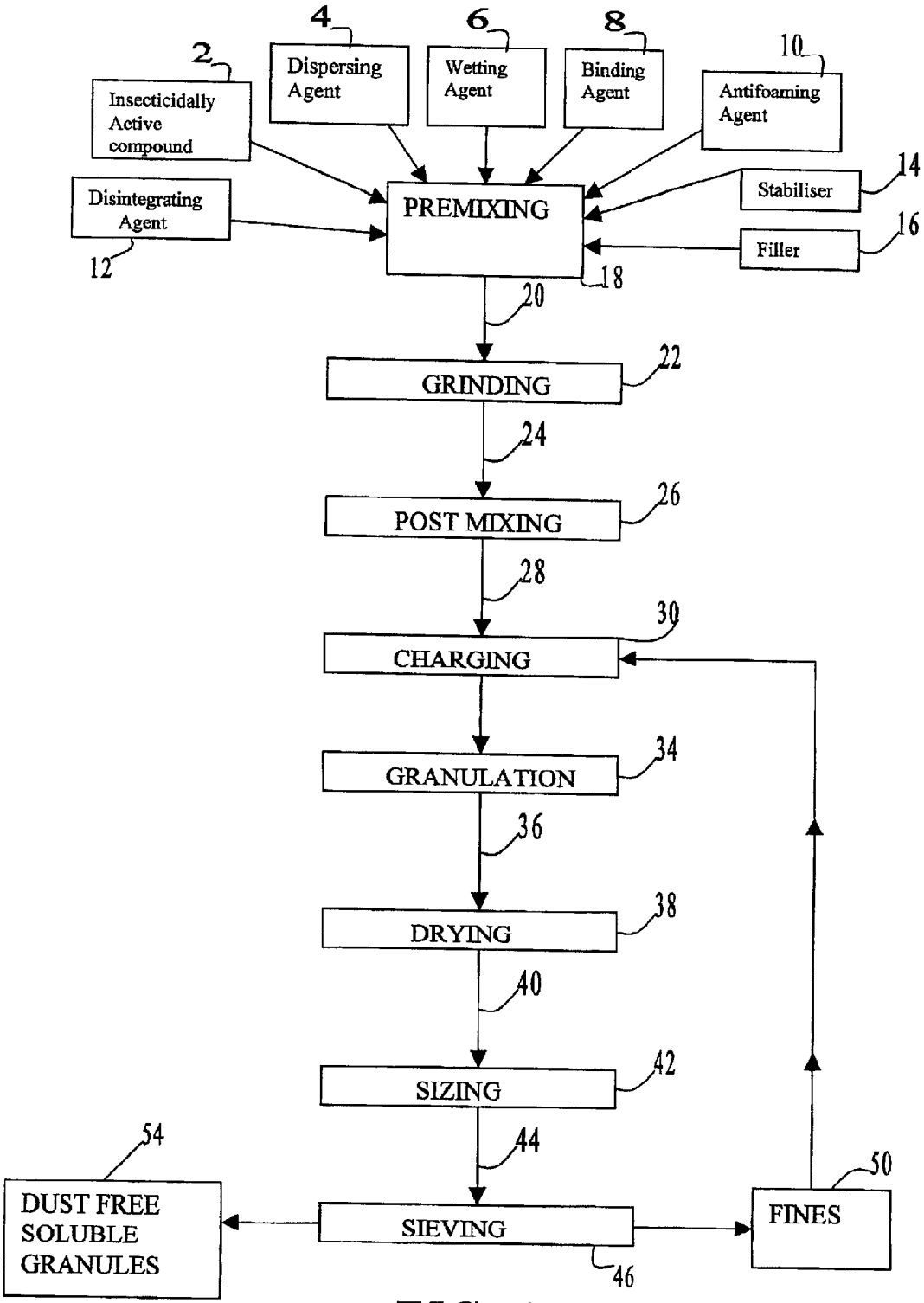


FIG. 1

PROCESS FOR PREPARATION OF CHEMICALLY STABLE, DRY-FLOW, LOW COMPACT, DUST FREE, SOLUBLE GRANULES OF PHOSPHOROAMIDOTHIOATES

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit, under 35 U.S.C. 119(e), of U.S. Provisional Application No. 60/340,272 filed Dec. 18, 2001, the contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for preparing insecticidally active soluble granules of phosphoroamidothioate, referred to herein as acephate.

2. Background Information

In recent years, agricultural chemicals have been most preferably formulated in the form of dusts, wettable powders, soluble powders, emulsifiable concentrates, soluble liquid/concentrates, granules, coated granules, water dispersible granules, suspension concentrates, and solutions. Occasionally, when dusts are produced by absorbing or mixing active ingredients with a finely divided inert carrier material, for example China Clay or the like, drift problems occur. With wettable powders and soluble powders the problems faced at the time of dilution are not only drift, but the final disposal of containers, for dust particles tend to stick to sides of the containers. The left over materials within the containers pose great problems to the environment, operators and users.

Although dusts are undesirable because of airborne contamination and handling difficulties, liquid spray formulations have not provided an acceptable alternative, for they involve solvents and packaging expenses, along with container disposal requirements that detract from their commercial desirability.

Water dispersible granules produced by fluidized bed spray dryers overcome the problems associated with wettable powders and soluble powders, but have high processing costs and require high value capital investment, as well as requiring highly skilled staff. These problems impose a significant barrier in widening the market acceptance of these compounds.

Certain phosphoroamidothioates and phosphoroamidodithioates, collectively referred to as Phosphoroamidothioates, are known to have excellent insecticidal activity against a variety of insects and in a variety of environments. Acephate, one of the important commercial insecticides within this class of compounds, is a systemic and contact insecticide of moderate persistence with residual activity lasting about 10–15 days. It is effective against a wide range of aphids, leaf-miners, lepidopterous, larvae, sawflies and thrips and it is also a non-phytotoxic on many crop plants.

Phosphoroamidothioate containing pellets have been proposed in the past, but difficulties have been encountered in pelletizing acephate technical, the preferred insecticide within the class of phosphoroamidothioates. Attempts to manufacture acephate technical pellets from acephate technical powders have been proposed and have been unsuccessful.

Considerable experimentation in the area of producing the preferred high-strength acephate granules has been conducted and confirms the manufacturing difficulties which

lets and methods proposed for making pellets suggested in the prior art leave considerable room for improvement. Prior extrusion processes have proposed the addition of costly surfactants, the combination of phosphoroamidothioate with a second active ingredient, or the creation of a mixture of the active ingredient with a solvent in an amount of from 3–25% by weight before extrusion, but these processes have not solved the problems encountered.

The formulation of acephate presently in use is acephate 75% soluble powder having acephate active ingredient 75% (w/w), surfactant 1 to 2% (w/w), inert filler (precipitated silica) to make 100% (w/w). Acephate 75% soluble powder poses the problems of dust, low pourability, high transportation costs, high capital manufacturing investment, measurement difficulties, difficulties in packing material disposal, handling problems, high risk of caking and others.

Because of the problems associated with producing granular forms of phosphoroamidothioates, such as the preferred acephate, there is a need in the art for a process for preparing chemically stable, dry flow, low compact, dust free, insecticidally active soluble granules of phosphoroamidothioate which are useful from a practical stand point, as well as for a low cost, practical manufacturing technique which can be practiced on a commercial scale without requiring expensive additives or solvents.

SUMMARY OF THE INVENTION.

By the present invention the above-identified major limitations have been overcome. The method for producing dry flow, low-compact, dust free, soluble phosphoroamidothioate granules, such as the preferred compound acephate, is an improvement over prior manufacturing processes. Further, the dust free soluble granules produced by this invention, which has a concentration of the insecticidally active ingredient in this formulation may vary from 40–98% of phosphoroamidothioate active ingredient, is more advantageous than prior granular products and exhibits certain very desirable characteristics as noted hereinafter.

Briefly, and in accordance with a preferred embodiment of the invention, dry flow, low compact, dust free, soluble granules of insecticially active phosphoroamidothioate are prepared by forming a pre-mix containing the required quantity of phosphoroamidothioate, a dispersing agent, a wetting agent, a binding agent, an antifoaming agent, a disintegrating agent, a stabilizer and filler. The specified adjuvants have a maximum of 1% water insoluble matter. This pre-mix is then ground to produce a ground product having preferred particle sizes between 5.0 microns to 10.0 microns. The ground product is fed to a post-mixer to form a mixture. The mixture is then fed through a hopper into a granulator where granules are formed. The granules are then dried, and the dried granules are sized and sieved to separate dry granules from fines, producing dry flow, low compact, dust free, soluble granules of phosphoro-amidothioate as noted above, the preferred phosphoroamidothioate is acephate. The fines may be recycled back to the post mixer.

This invention produces essentially dry flow, low compact, dust free soluble phosphoroamidothioate granules having a preferred granule size of 1.5 to 3.0 mm in length and 0.5 to 1.0 mm in diameter. These granules of phosphoroamidothioates are characterized by aging stability for a minimum of two years.

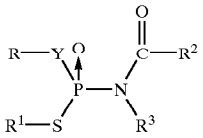
BRIEF DESCRIPTION OF THE DRAWINGS

The features and advantages of the present invention will become apparent from the following detailed description of preferred embodiments thereof, taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a flow chart of the preferred embodiment of the

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention is best described by referring to the flow chart in FIG. **1**. An essentially dry pre-mix comprising about 95% to 99% of solids and 1% to 5% moisture and/or solvent is formed from the following ingredients: 40% to 98% of the insecticidally active compound **2**, 0.1% to 5.0% dispersing agent **4**, 0.1% to 3.0% wetting agent **6**, 0.1% to 3.0% binding agent **8**, 0.01% to 0.08% antifoaming agent **10**, 0.01% to 10.0% disintegrating agent **12**, 0.01% to 1.0% stabilizer **14**, and fillers **16** to make 100% (w/w). The insecticidally active compounds of the present invention have the following formula:



wherein R and R^1 individually are an alkyl, alkenyl or alkynyl group containing upto 6 carbon atoms, R^2 is hydrogen, an alkyl group containing 1 to 18 carbon atoms, a cycloalkyl group containing 3 to 8 carbon atoms, an alkenyl group containins 2 to 18 carbon atoms or an alkynyl group containing 3 to 18 carbon atoms, R^3 is hydrogen or an alkyl group containing 1 to 6 carbon atoms, and Y is oxygen or sulfur. All of the inert ingredients are preferably solids and in a powder form. In one preferred embodiment, the binding agent **8** is selected from sucrose and starch derivatives or a blend thereof, the wetting agent **6** is selected from calcium or sodium salt of alkyl aryl sulphonate, the dispersing agent **4** is selected from the derivative of sulfonated fatty alcohols, the disintegrating agent **12** is selected from swelling type clays such as Bentonite and zeolite, the antifoaming agent **10** is selected from silicon oil derivatives, the stabiliser **14** is selected from salts of higher fatty acids, and the filler **16** is selected from precipitated silica and kaoline and the like. Grinding **22** of the pre-mix **20** is then conducted, preferably in a microniser, to obtain a ground product **24** having a preferred particle size of 5 microns to 10 microns.

The ground product **24** is subjected to post-mixing **26** to form a mixture **28** which is then made into granules **36** by preferably charging **30**, by way of a rotary feeder, a feeding hopper which supplies the mixture to a granulator for granulation **34**. The granulator that performs the granulation **34** has a preferred inlet temperature between 30 to 35° C. and a preferred outlet temperature of between 40° C. to 45° C. The resulting granules **36** are subjected to a drying **38** process, preferably by passing the granules **36** through an air chamber, producing dry granules **40**.

Sizing **42** the dry granules **40** is then accomplished to produce sized granules **44** of a desired length and diameter. Sizing the granules is preferably conducted by passing the dry granules **40** through an oscillating cutter to obtain granules which are preferably between about 1.5 mm and 3.0 mm in length and 0.5 mm to 1.0 mm in diameter. After sizing, the sized granules **44** are subjected to sieving **46** to separate fines **50** generated during the sizing process from desired dust free soluble granules **51**.

The fines **50** from the sieving **46** process may be collected and recycled at the charging **30** stage of the process to obtain a minimum yield of 99.0% dry flowable, low compact, dust free, soluble granules **54** of phosphoroamidothioates, preferably acephate.

The dust free soluble granules **54** were tested for required quality specifications and packed in desired packing. This soluble granules **54** enjoy all the formulation advantages described above, producing dust free soluble granules **54** which are beneficial from an economic aspect and a handling aspect and which show a very good performance during use.

The following examples are presented to illustrate but not to restrict the present invention. Parts and percentage are by weight unless otherwise specified.

EXAMPLE 1

Acephate 97% Granules can be prepared as follows:

Composition

Ingredients	Quantity (% w/w)
Acephate Technical 98.5% purity	98.48
Dispersing agent	0.50
Wetting agent	0.10
Binding agent	0.10
Antifoaming agent	0.03
Disintegrating agent	0.50
Stabilizer	0.05
Filler	0.24
Total	100.00

EXAMPLE 1 PROCESS

The constituents of the above composition are mixed in a pre-mixer, then ground in a microniser to the required size of 5 micron to 10 micron. The ground product **24** is again mixed in a post-mixer to get a uniform homogeneous mixture **28**. This homogeneous mixture **28** is then fed through a rotary feeder into a low compaction granulator, while maintaining an inlet temperature of 32 to 35° C. and an outlet temperature of 40 to 45° C. The Acephate granules **36** formed in the granulator are further dried through an air chamber, sized to 1.5 mm to 3 mm length, and are collected. The fines **50** generated during the process are recharged to get a conversion yield of 99 percent.

EXAMPLE 2

Acephate 98% granules can be prepared as follows:

Composition

Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	99.50
Dispersing agent	0.25
Wetting agent	0.03
Binding agent	0.05
Antifoaming agent	0.02
Disintegrating agent	0.05
Stabilizer	0.05
Filler	0.05
Total	100.00

Acephate 98% granules with above composition can be prepared by following the process described in EXAMPLE

EXAMPLE 3

Acephate 97.5% granules can be prepared as follows:

Composition

Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	98.99
Dispersing agent	0.40
Wetting agent	0.10
Binding agent	0.10
Antifoaming agent	0.03
Disintegrating agent	0.20
Stabilizer	0.05
Filler	0.13
Total	100.00

Acephate 97.5% granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 4

Acephate 90% Granules can be prepared as follows:

Composition

Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	91.38
Dispersing agent	00.75
Wetting agent	00.10
Binding agent	00.20
Antifoaming agent	00.03
Disintegrating agent	01.00
Stabilizer	00.50
Filler	06.04
Total	100.00

Acephate 90% granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 5

Acephate 85% granules can be prepared as follows:

Composition

Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	86.30
Dispersing agent	01.50
Wetting agent	00.50
Binding agent	01.00
Antifoamer	00.05
Disintegrating agent	02.00
Stabilizer	00.60
Filler	08.05
Total	100.00

Acephate 85% granules with above composition can be prepared by following the process described in EXAMPLE

EXAMPLE 6

Acephate 75% Granules can be prepared as follows:

Composition

Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	76.15
Dispersing agent	2.00
Wetting agent	1.50
Binding agent	1.50
Antifoaming agent	0.06
Disintegrating agent	5.00
Stabilizer	0.75
Filler	13.04
Total	100.00

Acephate 75% Granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 7

Acephate 50% Granules can be prepared as follows:

Composition

Ingredients	Quantity (% w/w)
Acephate Technical 98.5% purity	50.77
Dispersing agent	3.00
Wetting agent	2.00
Binding agent	3.00
Antifoaming agent	0.08
Disintegrating agent	10.00
Stabilizer	1.00
Filler	30.15
Total	100.00

Acephate 50% Granules with above composition can be prepared by following the process described in EXAMPLE 1.

EXAMPLE 8

Acephate 40% granules can be prepared as follows:

Composition

Ingredient	Quantity (% w/w)
Acephate Technical 98.5% purity	40.61
Dispersing agent	4.50
Wetting agent	3.00
Binding agent	3.00
Antifoaming agent	0.08
Disintegrating agent	12.00
Stabilizer	1.50
Filler	35.31
Total	100.00

Acephate 40% Granules of above composition can be prepared by following the process described in EXAMPLE 1.

Tests

The physical properties of Acephate granules were determined before and after aging at 45° C. for 500 hrs and for

DOCKET ALARM

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts

Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research

With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips

Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS
Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS
Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS
Sync your system to PACER to automate legal marketing.