

**United States Patent** [19]

Chan et al.

[11] Patent Number: **5,075,058**

[45] Date of Patent: **Dec. 24, 1991**

[54] **PROCESS FOR PREPARING PELLETS COMPRISING INSECTICIDAL N-HYDROCARBOYL PHOSPHOROAMIDOTHIOATES AND/OR PHOSPHOROAMIDODITHIOATES, AND FUNGICIDES, HERBICIDES, FERTILIZERS OR OTHER INSECTICIDES**

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[21] Appl. No.: **472,353**

[22] Filed: **Jan. 30, 1990**

[51] Int. Cl.<sup>5</sup> ..... **B29B 9/08**

[52] U.S. Cl. .... **264/118; 264/141; 424/405; 424/408; 424/489; 514/120**

[58] Field of Search ..... **264/118, 141, 142, 143, 264/117; 71/64.04; 424/408, 489, 405; 514/120**

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[57] **ABSTRACT**

A method of making insecticidal pellet compositions of N-hydrocarboyl phosphoroamidothioates and phosphoroamidodithioates, combined with a herbicide, fungicide, fertilizer or other insecticide is provided.

**11 Claims, No Drawings**

PROCESS FOR PREPARING PELLETS  
COMPRISING INSECTICIDAL  
N-HYDROCARBOYL  
PHOSPHOROAMIDOTHIOATES AND/OR  
PHOSPHOROAMIDODITHIOATES, AND  
FUNGICIDES, HERBICIDES, FERTILIZERS OR  
OTHER INSECTICIDES

The present invention is directed to a method of making pelletized insecticidal N-hydrocarboyl phosphoroamidothioates and/or and phosphoroamidodithioate formulations containing fungicides, herbicides, fertilizers or other insecticides.

BACKGROUND OF THE INVENTION

Certain N-hydrocarboyl phosphoroamidothioates and phosphoroamidodithioates have high insecticidal activity. A particularly important commercial insecticide within these classes of compounds is the insecticide ORTHENE®, which can be systemically taken up by a plant so that insects which feed and/or live on the plant are killed, in addition to those insects which directly ingest or are contacted by the insecticide. See U.S. Patent Nos. 3,716,600, 3,845,172 and 3,914,417. ORTHENE® is commercially produced as technical grade chemical of about 97 to 99.5% purity. One method of formulating technical grade ORTHENE® for commercial use is to mix the technical grade powder with an anti-caking agent, such as fumed silica, and a wetting agent. The wetting agent is utilized to assist the wetting of silica (if present) and to improve the spread-out of ORTHENE® and the anti-caking agent is used to prevent agglomeration of the ORTHENE® in its container.

The wetting agent is utilized to assist the wetting of silica (if present) and to improve the spread-out of ORTHENE® when it is applied to crops as a spray solution, or when applied as a dust, after exposure to moisture via rain, dew, or irrigation. The powdered commercial forms of ORTHENE® are available in dilutions referred to as ORTHENE® 90S, ORTHENE® 75S, ORTHENE® 50S, and in other commercial dilutions.

The powder form allows formulations of ORTHENE® to relatively high concentrations, e.g., ORTHENE® 90S. Other, lower concentrate formulations are targeted to discrete markets using a soluble powder signified as -xxS. In most cases, the application of ORTHENE® XXS to the crop is via a water solution spray. The anti-caking agents, while promoting product flowability during the solution/mixing process, do not enhance the solution method of application. On the other hand, inherent to all powders, handling difficulties due to dust make this form of product less desirable than liquids and agglomerate forms. Furthermore, ORTHENE® has a characteristically mercaptan odor (believed to be organothio compounds) which is compounded by the problems with dust.

ORTHENE® is available in liquid form, which minimizes or eliminates airborne contamination due to dust. However, due to solubility and storage stability limitations of solutions, its concentration is limited to a maximum of 25%, the balance being solvent and adjuvants. ORTHENE® in a liquid formulation has a solvent and packaging expense as well as a container disposal requirement that makes it less attractive to the

consumer on the basis of price and empty container disposal requirements.

An agglomerate form of ORTHENE® which also minimizes airborne contamination due to dust, has been constrained to dilute concentrations of ORTHENE® applied to large particles by spraying and then dried, or as a dilute concentration of ORTHENE® combined with binders and anti-caking agents to form agglomerates via processes known to those skilled in the art, such as, pan granulation, extrusion, fluid granulation, pelletizing. The concentration of ORTHENE® via these methods has heretofore been limited to a concentration no greater than about 36% to 50%, with known commercial products typically no more than 5% ORTHENE. The limit on concentration of ORTHENE® was due to the melt property of ORTHENE® limiting the feasible operability of this form of product. Concentration of active ingredient is further limited by the ability of binding agents to form agglomerates, i.e. a minimum amount of any particular binding agent is required in order to meet physical properties of attrition resistance, crush strength and bulk density. In the case where liquid ORTHENE® solutions were sprayed on agglomerates and then dried, the limitation of concentration was due to the practical wetting ability of the receiving agglomerate. Too much liquid applied would form a mud. At these low levels of ORTHENE® concentration, commercial products are more costly to produce and are not suitable for applications of ORTHENE® made via solution spraying.

The ORTHENE® xxS formulations have problems due to the inorganic anti-caking agent ingredients. These anti-caking agents are not soluble in water (the typical application spray solvent) or other normal solvents. Due to their insolubility, they can settle in the applicator's spray tank. The settled anti-caking agents plug spray nozzles which detracts from the marketability of the ORTHENE® xxS product line. This spray nozzle plugging problem can occur when ORTHENE® xxS products are tank mixed with other commercial pesticides, which is a normal farming industry practice. While methods to minimize the occurrence of anti-caking agent settling have evolved, they require special procedures to avoid nozzle plugging conditions, which adds to the inconvenience of using ORTHENE® xxS.

Furthermore, an anti-caking agent(s) segregates in the manufacturing process equipment during material handling procedures and forms insoluble bits of anti-caking agent which can cause spray nozzle plugging. This may lead to inconsistent application of the correct amount of active ingredient.

Therefore, alternative forms to ORTHENE® powders, that resolve problems characteristic of dusts are desired by both the manufacturer and the marketplace. One possible alternative to a powdered ORTHENE® is in the form of a pellet: a cylindrically shaped solid. Pellets practically eliminate the dust problems and reduce the surface area-to-weight ratio which mitigates the odor problem.

However, currently available granular ORTHENE®, as mentioned above, contains relatively small amounts of ORTHENE®, typically no more than 5% active ingredient. Attempts to manufacture technical assay (approximately 97% active ingredient) ORTHENE® pellets from the dry ORTHENE® technical powder have heretofore been unsuccessful. The anti-caking agents and binders needed to make the currently



of deodorants and anti-foam agents may also be used as additives.

As discussed above, it is a particular advantage of the present invention to provide pelletized compositions which contain active ingredients in addition to the insecticidal composition described above. In particular, it will particularly advantageous to combine the ORTHENE® insecticides in a pellet with other insecticides, particularly pyrethroid insecticides such as DECIS™ (also known as deltamethrin, melting point 98°-101°C.), PYDRIN™ and ASANA™ (Fenvalerate), DANITOL™, CASCADE™ (Flufenoxuron), DURSBAN™ (chlorpyrifos), DIBROM™ ("Naled"), etc. Most of these insecticides are solids, thus to prepare a pellet with ORTHENE® they are preferably milled, if necessary, to fine particle grain size (1-8 microns average diameter), and mixed with a solid dispersant, solid wetting agent, and/or solid surfactant. A particularly preferred composition is a mixture of 13:1 ORTHENE® to ASANA™ containing 6% by weight of Morwet™ D425 dispersant; 0.5% wetting agent and 7% Unithox™ 480 surfactant formed into pellets.

Some of the above insecticides are liquids, such as PYDRIN™ (yellow liquid, melting point 23° C.). In such cases the liquid may be first absorbed onto a carrier such as a diatomaceous earth (such as Celatom™) and then the two solids (the ORTHENE® and the PYDRIN™ saturated Celatom™) may be mixed with a solid dispersant, solid wetting agent and solid surfactant.

In some instances, the second insecticide, such as DANITOL™ is highly toxic and therefore to alleviate the hazard of handling the pellets, the DANITOL™ may first be encapsulated by mixing with a surfactant such as Pluronic® series (F-108) Tetric™ series (such as 908), Unithox™ series (such as 480, 550 or 520) by milling the DANITOL™ with the surfactant. The ORTHENE® is then mixed with the milled DANITOL™ /surfactant and pelletized in a pellet mill.

Similarly, solid or liquid fungicides, herbicides, or fertilizers may be pelletized with the ORTHENE® in accordance with the methods described above.

In addition, in some instances, particularly when a fertilizer is an active ingredient, the direct contact of the ORTHENE® insecticide with the fertilizer (or fungicide, herbicide or other insecticide) may chemically degrade the ORTHENE® or vice versa, thereby detracting from the desired activity of the pellet. In such instance each of the active ingredients may be pelletized separately and then blended thereby retaining the stability of each of the active ingredients. For example, KOCIDE™ (copper hydroxide) is not chemically compatible with ORTHENE® and therefore first, KOCIDE™ /Unithox™ 480 pellets may be made into a stable combination, then it is combined with ORTHENE® pellets to form a stable physical insecticide/fungicide formulation. Other fungicides include SPOTLESS™, FOLPET™, CAPTAN™, etc. Herbicides which may be utilized include DEURINOL™, DURNOL™, ODRAM, SURFLAN™, BENCHMARK™, SELECT™, etc. Fertilizers include various formulations of NPK fertilizers such as 23-19-17, etc.

In some instances, the physical dry mixture from which the pellets are formed will need to be intimately mixed by evaporation from a solution. For example, ORTHENE® can be protected by a surfactant by first

mixing ORTHENE® and a surfactant such as Unithox™ 480 (typically 1:4 ratio) to form a solution in methylene chloride, alcohol, or water. By evaporation of the solvent, the remaining solid may be ground and sieved to an appropriate size (such as 20 mesh). Then the dry powder may be mixed with a solid fertilizer (such as 23-19-17) and pelletized as described above. In this instance the ORTHENE® is protected from the fertilizer by the surfactant.

In the most preferred embodiment according to the present invention the pellets are made by forming a dry, extrudable mixture of the solid technical insecticide composition and the other active ingredients, optionally containing other dry additives described above. The dry ingredients should be ground or provided in a powdered form. In some instances a diluent such as ammonium sulfate will also be utilized usually in an amount less than about 5% and usually around 1% by weight of the total composition. No solvent is added to this composition. However, it is realized that many commercial versions of surfactants contain small amounts (typically about 2% by weight of the surfactant) of moisture. The presence of such moisture is not deleterious to the preparation of the pellet, and the pellet may be later dried, if desired.

As the extrusion product exits the extruding orifice, the product is cut to appropriate size, usually about 3 mm to 10 mm in length. Useful pellets will be extrudates of about 3 mm to 25 mm in length with diameters from about 1.5 mm to 7 mm. Spherical pellets are also useful having diameters of about 1 mm to 5 mm.

#### EXAMPLE 1

In a Hobart (C-147) mixer 171g of ASANA™ tech (75%) insecticide was added slowly to 243g Celatom™ MN-47 diatomaceous earth. After mixing for 15 minutes 165g of Morwet™ D-425, 15g of Morwet™ EFW (dispersants) were added. This was mixed with 210g Unithox™ 480 (surfactant), 2196g ORTHENE® Tech (98%) and 1.5g of an anti-foam agent (Antifoam A). The mixture was screened to break-up lumps of the insecticides, then extruded into pellets.

#### EXAMPLE 2

A pre-mix consisting of 177g. SPOTLESS™ Tech (81%), 165g. Morwet™ D-425 and 45g. Morwet™ EFW were mixed in a Hobart mixer. This pre-mix was then mixed with 2463g ORTHENE® Tech (98%), 150g Unithox™ 480 and 1.5g Antifoam A. The mixture was extruded into pellets at about 100° F.

#### EXAMPLE 3

In a Hobart mixer 210 DIBROM™ (insecticide) was added to 300g Celatom™ and mixed for 15 minutes. This premix was then mixed with 2100g ORTHENE® Tech (98%), 165g Morwet™ D-425, 15g Morwet™ EFW, 210g Unithox™ 480 and 1.5g Antifoam A. The mixture was extruded into pellets at about 91° F.

#### EXAMPLE 4

To a pre-mix containing 2700g Fertilizer 23-19-17 and 240g Unithox™ 480 were added 60g ORTHENE® Tech (97%) and 1.5g Antifoam A. The mixture was extruded to 3/32" pellets in a California Pellet Mill, then dried.



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