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16381/88

AUSTRALIA

CONVENTION

Patents Act

APPLICATION FOR A STANDARD PATENT

I/We The Dow Chemical Company

of 2030 Dow Center,
Abbott Road,
Midland,
Michigan 48640,
UNITED STATES OF AMERICA.

AMENDMENT ACCEPTED AND AMENDMENTS

17-7-90

hereby apply for the grant of a standard patent for an invention
entitled:

COMPOSITION AND METHOD OF STABILIZING
O-HALOPYRIDYLPHOSPHATES

which is described in the accompanying complete specification.

Details of basic application

Number of basic application: 015,769

Convention country in which
basic application was filed: UNITED STATES OF AMERICA

Date of basic application : 17 February 1987

LODGED AT SUB-OFFICE

19 JAN 1988

Melbourne

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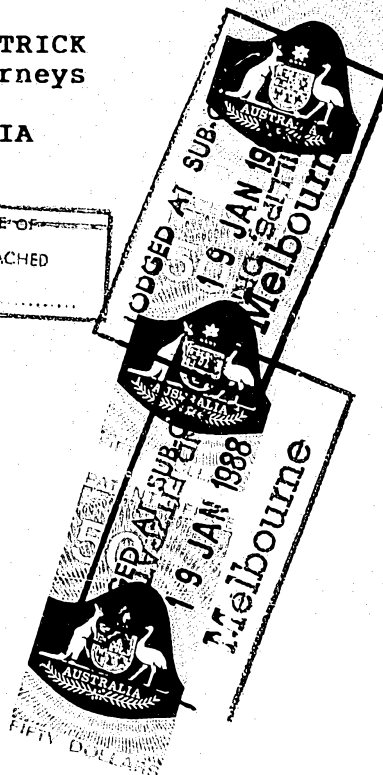
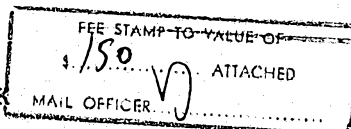
Dated: 18 January 1988

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
The Dow Chemical Company

By:

Our Ref : 81545
POF Code: 1037/1037

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AUSTRALIA

Patents Act

35,477-F

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AUSTRALIA
Patent Declaration

DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS

(a) Insert "Convention"
if applicable
(b) Insert FULL name(s)
of applicant(s)

(c) Insert "of addition"
if applicable
(d) Insert TITLE of
invention

(e) Insert FULL name(s)
AND address(es) of
declarant(s)
(See headnote*)

(f) Insert FULL name(s)
AND address(es) of
actual inventor(s)

(g) Recite how appli-
cant(s) derives
title from actual
inventor(s)
(See headnote**)

(h) Insert country,
filing date, and
basic applicant(s)
for the/or EACH
basic application

(k) Insert PLACE of
signing

(l) Insert DATE of
signing

(m) Signature(s) of
declarant(s)

Note: No legalization or
other witness required

In support of the (a) Convention application made by

(b) THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, United States of America

(hereinafter called "applicant(s)" for a patent (c) for an
invention entitled (d)

COMPOSITION AND METHOD OF STABILIZING O-HALOPYRIDYLPHOSPHATES

I/We (e) Richard G. Waterman, General Patent Counsel
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, United States of America
do solemnly and sincerely declare as follows:

1. ~~I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/We are authorized to make this declaration on behalf of the applicant(s).

2. ~~I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

2. (f) ROY L. VAN HORN, 5400 S. M-30; Beaverton, State of
Michigan 48612, United States of America

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s)
is/are entitled to make the application are as follows:

(g) The applicant Company is the assignee of the said
invention from the said actual inventor(s).

(Note: Paragraphs 3 and 4 apply only to Convention applications)

3. The basic application(s) for patent or similar protection on which the application is based
is/are identified by country, filing date, and basic applicant(s) as follows:

(h) Priority Serial No.: 015,769

Filing Date: February 17, 1987

Inventor: Roy L. Van Horn

Country: UNITED STATES OF AMERICA

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s)
made in a Convention country in respect of the invention the subject of the application.

Declared at (k) Midland, Michigan, 48640,

Dated (l) January 4 1988 U.S.A.

(m) THE DOW CHEMICAL COMPANY

CORP.
SEAL

To: The Commissioner of Patents

By:

RICHARD G. WATERMAN
General Patent Counsel

Agent: Phillips, Ormonde & Fitzpatrick

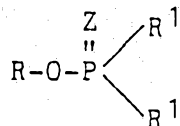
No legalization or other
witness required

(12) PATENT ABRIDGMENT (11) Document No. AU-B-10381/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 602046

- (54) Title
COMPOSITION AND METHOD OF STABILIZING O-HALOPYRIDYLPHOSPHATES
- International Patent Classification(s)
(51)⁴ **A01N 057/32 A01N 025/22 A01N 057/16**
- (21) Application No. : **10381/88** (22) Application Date : **19.01.88**
- (30) Priority Data
- (31) Number (32) Date (33) Country
015769 17.02.87 US UNITED STATES OF AMERICA
- (43) Publication Date : **18.08.88**
- (44) Publication Date of Accepted Application : **27.09.90**
- (71) Applicant(s)
THE DOW CHEMICAL COMPANY
- (72) Inventor(s)
ROY L. VAN HORN
- (74) Attorney or Agent
PHILLIPS ORMONDE & FITZPATRICK, 367 Collins Street, MELBOURNE VIC 3000
- (56) Prior Art Documents
US 3224586
AU 55346/86 A01N 57/16, 57/32 C07D 213/64, 213/73
EP 185282
- (57) Claim

1. A composition comprising:

(a) an insecticidally-effective amount of an O-halopyridylphosphate insecticide of the formula:



wherein R represents halopyridyl, Z represents oxygen or sulfur, and each R¹ represents lower-alkoxy, amino or loweralkylamino, wherein said insecticide is admixed with an amount effective to thermally stabilize the insecticide of

(b) a carrier which is a wood flour, a hemicellulose extract, a mixture of wood flour and a diatomaceous earth, or a mixture of wood flour and a kaolinite clay.

(11) AU-B-10381/88
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9. A method for protecting stored grain or non-crop areas or plants from insect-damage comprising applying to the locus of the grain or plants the composition of any one of Claims 1 to 8.

602046

COMPLETE SPECIFICATION
(ORIGINAL)

Application Number:	Class	Int. Class
Lodged:		

Complete Specification Lodged:
Accepted:
Published:

This document contains the amendments made under Section 49 and is correct for printing.

Priority

Related Art:

APPLICANT'S REFERENCE: 35,477-F

Name(s) of Applicant(s):

The Dow Chemical Company

Address(es) of Applicant(s):

2030 Dow Center,
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UNITED STATES OF AMERICA.

Address for Service is:

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Complete Specification for the invention entitled:

COMPOSITION AND METHOD OF STABILIZING O-HALOPYRIDYLPHOSPHATES

Our Ref : 81545
POF Code: 1037/1037

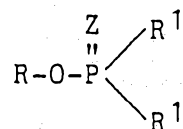
The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

COMPOSITION AND METHOD OF STABILIZING
O-HALOPYRIDYLPHOSPHATES

This invention relates to a novel composition and method for stabilizing O-pyridyl phosphate insecticides.

More particularly, the invention provides a composition comprising:

(a) an insecticidally-effective amount of an O-halopyridylphosphate insecticide of the formula:



wherein R represents halopyridyl, Z represents oxygen or sulfur, and each R¹ represents lower-alkoxy, amino or loweralkylamino, wherein the insecticide is admixed with

(b) a carrier which is a wood flour, a hemicellulose extract, a mixture of wood flour and a diatomaceous earth, or a mixture of wood flour and a kaolinite clay wherein the wood flour or hemicellulose extract is in an amount effective to

thermally stabilize the insecticide. The invention is also directed to a method for protecting stored grains and plants from insect damage by utilizing the compositions. Preferably, the carrier is a wood flour or a mixture of a softwood flour and a diatomaceous earth. Most preferably the wood flour is a softwood flour.

In this application, the terms "powder", whether high or low concentrate, and "compositions" are used interchangeably and have the same meaning.

The terms "loweralkoxy" and "loweralkylamino" refer to alkoxy and alkylamino groups ^{preferably} having from 1 to 4 carbon atoms.

The preferred insecticide is "chlorpyrifos-methyl" which is O,O-dimethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate.

The O-halopyridylphosphate insecticide can be admixed with the desired carrier to make either high concentrate powders or low concentrate powders. Low concentrate powders are those which can be directly applied to control unwanted pests, i.e., those in stored grain or in storage facilities such as silos and storage bins without further preparation or dilution. High concentrate powders are those which can be admixed with additional carrier to prepare low concentrate powders. The concentration of the O-halopyridylphosphate in high concentrate powders can range from 10 to 95 percent (weight basis) or more, preferably from 30 to 90 percent, more preferably between 30 and 50 percent by weight insecticide. High concentrate powders can be admixed with additional carrier to



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prepare low concentrate powders. The concentrations of the O-halopyridylphosphate insecticide in low-concentrate powders can range from 0.5 to 10 percent (weight basis), preferable from 1 to 5 percent, most preferably 2 to 3 percent by weight insecticide. Thus in the compositions of the current invention the concentrations of O-halopyridylphosphate can range from 0.5 to 95 percent by weight.



~~prepare low concentrate powders. The concentrations of~~
the 0-halopyridylphosphate insecticide in low concen-
trate powders can range from 0.5 to 10 percent (weight
basis), preferably from 1 to 5 percent, most preferably
5 ~~2 to 3 percent by weight insecticide.~~

The term "wood flour" includes pulverized hard
woods, softwoods and mixtures thereof. Wood flour is
graded according to color and fineness. The particle
10 size of the wood flour can range from 2400 microns to 2
microns.

The term "softwood flour" includes pulverized
dried wood flour from softwood wastes or from softwood
15 manufacturing processes.

The term "hardwood flour" includes pulverized
dried wood flour from hardwood wastes or from hardwood
manufacturing processes.

20 The term "hemicellulose extract" refers to the
extract obtained by extracting water-soluble
hemicelluloses from the liquid stream of wood pulp
using steam and pressure. The extracted solution of
25 hemicelluloses is evaporated to a standard solids
content of about 57 percent. The hemicellulose is
largely free of lignin.

"Diatomaceous earth" refers to soft, bulky
30 solid material (about 88 percent or more silica)
composed of skeletons of small prehistoric aquatic
plants related to algae (diatoms).

"Barden Clay" is a kaolinite clay having an
35 average chemical analysis of about 45 percent silicon
dioxide (SiO_2) and 38 percent aluminum oxide (Al_2O_3).



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The wood flour or hemicellulose extract employed in the present method or composition should be an amount effective to stabilize the O-halopyridylphosphate insecticide from thermal degradation. In high concentrate powders, the wood flour or hemicellulose extract can comprise between 5 to 89 percent by weight of the total composition, preferably from 30 to 70 percent by weight, more preferably 50 to 70 percent by weight. In low concentrate powders, the wood flour or hemicellulose extract can comprise between 90 to 99.5 percent by weight of the composition, more preferably from 95 to 99 percent, most preferably 97 to 98 percent by weight of the total composition. Thus in the compounds of the current invention the concentrations of wood flour or hemicellulose extracts can comprise from 5 to 99.5 percent by weight of the composition.



~~The wood flour or hemicellulose extract~~
employed in the present method or composition should be
an amount effective to stabilize the O-halopyridyl-
phosphate insecticide from thermal degradation. In
5 high concentrate powders, the wood flour or
hemicellulose extract can comprise between 5 to 89
percent by weight of the total composition, preferably
from 30 to 70 percent by weight, more preferably 50 to
10 70 percent by weight. In low concentrate powders, the
wood flour or hemicellulose extract can comprise
between 90 to 99.5 percent by weight of the
composition, more preferably from 95 to 99 percent,
most preferably 97 to 98 percent by weight of the total
15 composition.

Where the carrier is a mixture of wood flour
and a mineral carrier such as a diatomaceous earth or a
kaolinite clay, the wood flour or hemicellulose extract
20 should be an amount effective to thermally stabilize
the insecticide. Generally the wood flour or
hemicellulose extract can be combined with the mineral
carrier in a ratio ranging from 20 to 1 part wood flour
to one part mineral carrier (weight basis), preferably
25 from 10 parts to 1 part wood flour to one part mineral
carrier, most preferably from 4 to 1.5 parts wood flour
to one part mineral carrier.

In situations where the carrier is wood flour
admixed with a mineral carrier such as kaolinite clay
or a diatomaceous earth, the composition of the present
invention can be prepared by admixing all components
together, in addition to any further addition of a
35 wetting agent and/or dispersing agent. Preferably, the
insecticide is uniformly admixed with the wood flour



and the mineral carrier is added to the wood flour admixed with insecticide.

5 The compositions of the present invention can be prepared by uniformly applying the O-halopyridyl-phosphate insecticide to the desired carrier to give the requisite insecticidal concentration in the compositions. Generally, the O-halopyridylphosphate insecticide is sprayed onto the carrier, and the
10 mixture of the insecticide and the carrier can be agitated until the insecticide is absorbed onto the carrier. The mixture can be ground to give a particular size ranging from 50 microns to 2400 microns, preferably about 50 microns.

15 In situations where the composition of the present invention are employed as wettable powders, the composition can be ground to a even finer particle size, which can range from 1 to 30 microns. Wetting
20 agents are added to the finely ground powder to improve its wettability when the powder is added to an aqueous medium. Such wetting agents include, but are not limited to, alkylnapthalene sulfonate salts and N-
25 -methyl-N-oleoyltaurate salts such as sodium, potassium or ammonium. Dispersing agents can be combined with the wetting agent to improve the dispersion of the powder when added to an aqueous medium. Typical
30 dispersing agents include the sodium based sulfonates of lignin and the salts of polymerized alkylnapthalene sulfonic acids. Typically, the wetting and dispersing agents can comprise between 3 to 10 percent (weight
35 basis) of the total insecticidal composition. The wetting and dispersing agents can be combined with the insecticidal compositions on its individual components according to any known methods.

Low concentrate powders of the present invention can be used in stored grain for protection of barley, oats, rice, sorghum and wheat against injury from stored grain weevils, moths, borers, beetles and mealworms including granary weevil, rice weevil, red flour beetle, confused flour beetle, saw-toothed grain beetle, Indian meal moth, Angoumois grain moth and lesser grain borer. The low concentrate powders can be applied to the grain at the rate of 0.128 to 0.64 kg/m³, preferably 0.128 kg powder per m³ as the grain is being loaded or turned into final storage. To protect stored grains from attack by Indian meal moth, the powder can be applied to the surface of clean or infested grain at the rate of about 0.034 kg/m² grain surface area.

The powder can be applied to the grain as evenly as possible, by any suitable means, such as sprinkling, blowing, laying, etc.

The low concentrate powders can be applied to grain in a truck or wagon prior to binning. The desired amount of the low concentrate powder is spread evenly over the surface of the grain in the truck or wagon. The powder can be mixed into the grain with any suitable utensil, such as a shovel. The powder becomes mixed with the grain as it is dumped from the truck or wagon into the hopper. Further mixing occurs when the grain is augered or blown into the bin. Mixing is completed as the powder and grain roll down the cone shaped pile in the bin.

High concentrate powders (10 to 90 percent by weight insecticide) can be admixed with additional

carrier to prepare the low concentrate powders discussed above.

5 Plants or plant parts can also be contacted with the compositions of the present invention in order to control insects such as crickets or grasshoppers. Such plants typically include vegetables such as tomatoes, cabbage, broccoli, lettuce or watermelons or field crops such as corn, soybeans, cotton, potatoes, 10 wheat or rice. The composition of the present invention can also be applied to non-crop plants in areas such as railroad right of ways. Sticker agents, which help the compositions to adhere more tightly to the grain or plant parts, can be added to the present 15 compositions. Such sticker agents include, but are not limited to, paraffinic oils, mineral oils such as white mineral oils, free and combined fatty acids, alkylaryl polyethoxyethanol, glycol ethers and di- 20 -alkylbenzene dicarboxylates.

Typically, the sticker agents can comprise from 3 to 10 weight percent of the total insecticidal composition. Such sticker agents can be combined with 25 the insecticidal composition or its individual components according to any known methods.

30 The following examples further illustrate the present invention. All parts are by weight unless otherwise specified.

Example 1 - Thermal Stability of Chlorpyrifos-methyl in Low Concentrate Powders

35 Fifteen grams (g) of a liquid insecticidal concentrate containing 60.6 percent (weight basis) chlorpyrifos-methyl and 39.4 percent aromatic solvents

were sprayed directly onto 285 g of various selected carriers to give prepared mixture calculated to contain less than 4 percent chlorpyrifos-methyl. The mixture was agitated on a rotating drum mixer for 10 minutes to ensure complete absorption of chlorpyrifos-methyl onto the carrier. The mixtures were then ground on a hammermill to give a uniform particle size of a nominal 50 mesh (297 microns). The ground samples were placed in a temperature controlled oven and heated to a temperature of 50 degrees Centigrade (°C) for a period of 60 and 90 days. A portion of the samples were analyzed for determining the amount of chlorpyrifos-methyl initially present (i.e., 0 days).

The percentages of chlorpyrifos-methyl remaining in the samples are presented in Table 1.

Table 1

Thermal Stability of Chlorpyrifos-methyl at 50°C (122°F) in Low Concentrate Dust Powders
Containing Less than 4 percent Chlorpyrifos-methyl

<u>Carrier</u>	Carrier and Solvent as Percent (%) of Formulation	Chlorpyrifos Methyl as Percent of Formulation	Percent Chlorpyrifos-methyl Remaining		
			<u>0 Days</u>	<u>60 Days</u>	<u>90 Days</u>
Softwood Flour	96.40	3.60	100.0	100.0	94.8
Hemicellulose Extract (Dried)	96.69	3.31	100.0	94.6	85.5
Softwood Flour (76%) + Diatomaceous Earth (19%)	96.99	3.01	100.0	100.0	100.0
Softwood Flour (76%) + Kaolinite Clay (19%)	96.39	3.61	100.0	100.0	90.3

The composition of the present invention can also be employed in non-crop areas (non-plant) such as households and industrial buildings including but not limited to restaurants, apartments, office buildings, warehouses and factories. Either high or low concentration powders with or without wetting agents, dispersing agents, sticking agents or mixtures thereof can be employed in such applications.

Example 2 - Thermal Stability of Chlorpyrifos in High Concentrate Powders

Essentially the same procedure was practiced as described in Example 1 except that molten concentrates of chlorpyrifos-methyl were employed in preparing the powders. Molten concentrates of chlorpyrifos-methyl heated to a temperature of 55°C were sprayed onto a preheated softwood carrier in a rotating blender to give chlorpyrifos-methyl concentrations ranging between 30 to 50 percent of the total composition. The percentages of chlorpyrifos-methyl remaining in the samples are presented in Table 2.

Table 2

Thermal Stability of Chlorpyrifos-methyl at 50°C (122°C) in High Concentrate Powders
Containing from 30-50 Percent Chlorpyrifos-methyl

<u>Carrier</u>	Carrier as Percent of <u>Composition</u>	Chlorpyrifos- methyl as Percent of <u>Composition</u>	Percent Chlorpyrifos-methyl Remaining After	
			<u>0 Days</u>	<u>60 Days</u>
Softwood Flour	58.2	41.8	100.0	90.3

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A composition comprising:

(a) an insecticidally-effective amount of an O-halopyridylphosphate insecticide of the formula:



10 wherein R represents halopyridyl, Z represents oxygen or sulfur, and each R¹ represents lower-alkoxy, amino or loweralkylamino, wherein said insecticide is admixed with an amount effective to thermally stabilize the insecticide of

15 (b) a carrier which is a wood flour, a hemicellulose extract, a mixture of wood flour and a diatomaceous earth, or a mixture of wood flour and a kaolinite clay.

20 2. The composition of Claim 1 wherein the O-halopyridylphosphate insecticide is chlorpyrifos-methyl.

25 3. The composition of Claim 1 wherein the concentration of O-halopyridylphosphate insecticide

in the composition is in the range from 0.5 percent to 95 weight percent and the carrier concentration is from 5 to 99.5 weight percent.

5 4. The composition of Claim 3 wherein the concentration of O-halopyridylphosphate insecticide in the composition is in the range from 2 to 3 percent and the carrier concentration is from 97 to 98 percent.

10 5. The composition of any one of Claims 1 to 4 wherein the carrier is a softwood flour.

15 6. The composition of any one of Claims 1 to 4 wherein the carrier is a mixture of a softwood flour and a diatomaceous earth.

20 7. The composition of any one of Claims 1 to 4 wherein the carrier is a mixture of a softwood flour and a kaolinite clay.

25 8. The composition of any one of Claims 1 to 7 further comprising an effective amount of (c) a wetting agent, a dispersing agent, a sticker agent or mixtures thereof.

30 9. A method for protecting stored grain or non-crop areas or plants from insect-damage comprising applying to the locus of the grain or plants the composition of any one of Claims 1 to 8.

~~DATED: 18 January 1988~~

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THE DOW CHEMICAL COMPANY

35



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10. A composition substantially as hereinbefore particularly described with reference to either one of the Examples.

DATED: 26 June 1990

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David Fitzpatrick

