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(54) Title: THERMALLY STABILIZED BIS ALKYLTHIO-ALKYLIMINO-N-ALKYL CARBAMATES

(57) Abstract

Sulfur-linked bis alkylthio alkylimino N-alkyl carbamate pesticides can be stabilized against thermal decomposition induced and accelerated by a variety of contaminants by incorporation of a substantially non-alkaline inorganic compound, containing at least two oxygen atoms bound to a multivalent cationic atom. Thermally stable wettable powder, dispersible granular and liquid formulations of these pesticides can be prepared.

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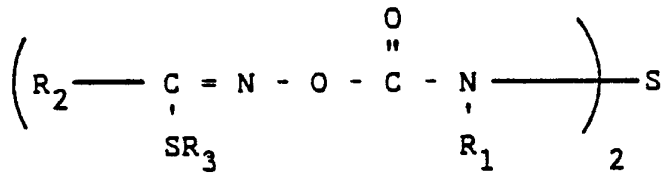
THERMALLY STABILIZED BIS ALKYLTHIO-ALKYLAMINO-N-ALKYL CARBAMATES

Field of the Invention

This invention relates to thermal stabilization of alkylthio-alkylimino carbamate pesticides. More particularly, it relates to the retardation or prevention of thermal decomposition of sulfur-linked bis alkylthio-alkylimino carbamates by incorporation of multioxygen inorganic compounds into formulations containing these pesticides.

Background of the Invention

Sulfur-linked bis alkylthio alkylimino-N-alkyl carbamate pesticides of the formula



have a wide range of uses in controlling insects and other agronomic pests. Active compounds exhibit a very high level of pesticidal activity and substantially reduced mammalian toxicity and phytotoxicity when compared to other pesticidal compounds having a comparable spectrum of activity against the above mentioned pests.

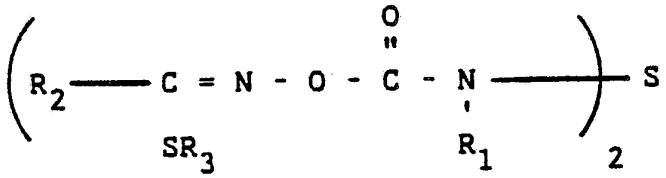
These compounds are thermally unstable in the presence of a variety of contaminants. Heavy metals and their salts, particularly chloride salts, are especially undesirable. Decomposition is extremely severe in the presence of copper metal,

copper chlorides, iron metal, iron chlorides and iron oxide in the form of rust. Other problematic metals include cobalt, nickel and aluminum. Concentrations of as little as 10 ppm are effective if given enough time at temperatures of 60°C or higher. Sulfur and sulfide salts can also induce decomposition, although usually at rates slower than those of chloride-containing systems. Some organic decomposition initiators have also been identified, including pyridine, pyridine hydrochloride, di- and trisulfides, amines, peroxides and acids (e.g. acetic and citric acids). Presence of 5% or more methomyl or its oxime can also induce decomposition.

The principal object of this invention to provide a method to inhibit or retard the thermal decomposition processes that may occur in bulk quantities of sulfur-linked bis alkylthio-alkylamino-N-alkyl pesticides when they are dried at elevated temperatures or stored for extended periods of time, especially in warmer climates. It is a further object to provide stable wettable powders and dispersible granular formulations of these pesticides.

Detailed Description of the Invention

This invention provides a method of retarding or inhibiting thermal decomposition of pesticides of the formula



(I)

wherein R_1 is alkyl containing from one to five carbon atoms; R_2 is alkyl, alkylthio, alkoxy, alkanoyl or alkoxycarbonyl, all of which may contain from one to five carbon atoms and which may be unsubstituted or aliphatically substituted in any combination with one or more cyano, nitro, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy or R_4R_5-NCO- groups; or R_2 is phenyl, R_4R_5-NCO- or $R_6CON(R_4)$, wherein R_4 and R_5 are individually hydrogen or alkyl, R_6 is hydrogen, alkyl or alkoxy; and R_3 is hydrogen, cyano, alkyl or alkylthio containing from one to five carbon atoms; provided that the total number of carbon atoms in R_2 and R_3 may not exceed eight and provided further that when R_2 is alkyl substituted with alkylthio, R_3 is alkyl, the inhibition or retardation of thermal decomposition of this compound being achieved by mixing the pesticide with from about 0.01% to about 95% by weight of a substantially non-alkaline inorganic compound containing at least two oxygen atoms bound to a multivalent cationic atom.

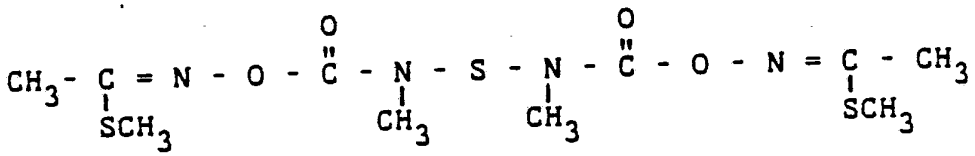
This invention also provides a pesticidal composition which comprises:
(a) a pestidically effective amount of a pesticide compound of the formula set forth above and (b) a substantially non-alkaline inorganic compound containing at least two oxygen atoms bound to a multivalent cationic atom, in an amount effective to retard or inhibit thermal decomposition of said compound.

A. Definitions

The term "powdered or granular composition" embraces all solid formulations which range in size from fine dusts (e.g., those which pass through U.S. Sieve screens No. 400 up to No. 100) to substantial particles as large as 5 mm in their largest dimension (e.g. those which pass through a No. 4 U.S. Sieve screen).

A "substantially non-alkaline inorganic compound" is one which, when dissolved or dispersed in water in an amount useful to this invention, does not create a pH greater than 9 or which can be buffered to a pH less than 9.

"Thiodicarb" is the generic name of a pesticide having the formula set forth below:



The term "compatability agent" encompasses additives that permit different pesticides to be combined in a single liquid formulation. Such agents may be incorporated into solid or liquid compositions containing one or all of the pesticides to be combined.

B. Pesticides

The organic compounds of this invention are alkylthio-alkylimino-N-alkyl carbamates. They are widely used to control a variety of insect pests. They may be prepared by well known methods, such as those set forth in U.S. Patents No. 4,004,031 and 4,382,957.

In the preferred compounds of this invention R_1 and R_3 or alkyl and R_2 is alkyl or alkylthio. The compound thiodicarb is especially preferred for the practice of this invention.

C. Thermodynamic Stability

Typical decomposition times for thiocarb in the presence of a variety of contaminants are shown in Table I. These data were collected using the following procedure. A one-gram sample of thiodicarb was intimately mixed with the indicated weight percent of contaminant. The solid was placed in a test tube that was then covered with a rubber septum cap and immersed in a constant temperature bath maintained at 100°C. An uncontaminated standard was run under similar conditions. Decomposition was manifested in a variety of forms. Some samples exhibited a rapid change from solid to dark liquid; dense yellow smoke was usually observed. Others underwent gradual discoloration and moistening. In these experiments the time of decomposition was the point when the sample was a dark-brown semi-solid. Reported values were averages of several repetitions for each sample.

The destabilizing effect of methomyl and other sulfur compounds is apparent from Section B

TABLE I

STABILITY OF CONTAMINATED THIODICARB STORED AT 100°C

Identity Contaminant	Amount of Contaminant	Time to Thiodicarb Decomposition at 100°C
A. Standard		
--		12-13 days
B. Autocatalytic Products		
Methomyl	1%	13 days
	5%	10 days
	10%	7 days
Methomyl oxime	5%	3 days
	10%	7 hours
Methyltrisulfide	1%	8 days
	3%	6 days
Dimethyl disulfide	1-3%	10 days
C. Miscellaneous Impurities		
$CuCl_2$	2 ppm	8-9 days
	2%	5 mins.
$FeCl_3$	3-300 ppm	8-9 days
	3%	10 mins.
	10%	45 sec.
Benzoyl peroxide	1%	5 days
	3%	3-5 days
Citric acid	1-3%	2 days
Acetic acid	1%	4-6 days
	3%	2 days
2-Ethylhexanoic acid	1-3%	6-10 days
Pyridine	1-3%	1-3 days

of Table I. Thiodicarb is stable at low concentrations (1% by weight or less) of one of its principal decomposition products, methomyl. However, as the concentration of methomyl is raised, the rate of decomposition increases significantly. Likewise, the effect of methomyl oxime is also substantial. As amounts of other decomposition products, such as dimethyltrisulfide and dimethyldisulfide increase, the rate of decomposition is substantially accelerated.

In Section C of Table I are included results of studies using contaminants that might be introduced during the preparation or storage of the pesticidal substance. As mentioned previously, heavy metal ions, particularly copper and iron, are especially deleterious. Use of manufacturing equipment or storage containers made of these metals in forms that can corrode to produce deleterious salts should be avoided if at all possible. The other organic materials are included to demonstrate the effects that such compounds might have on the product if they should be present, e.g. because they are found in the solvents that are used in the manufacturing process.

The ability of certain silicon-based carriers to reverse the decomposition of contaminated thiocarb is apparent from Table II. In these experiments one-gram samples of thiodicarb were first contaminated with the indicated weight percents of cupric and ferric chloride and then intimately mixed with a variety of silicas and silicates. The samples were then placed in test

tubes and immersed in water baths at 50°C, 70°C and 100°C until decomposition was observed; decomposition time was measured when the solid had turned into a dark brown liquid. All values represented averages of several repetitions. In some instances stabilization of several orders of magnitude was observed relative to standards containing no silica.

TABLE II

THIODICARB STABILIZATION BY SILICA-BASED CARRIERS

Contaminant	Stabilizer	Time to Decomposition at 50°C	70°C	100°C
--	--	>20 days	12 days	11-27 hrs.
1% $CuCl_2$	--	--	4 mins.	--
1% $CuCl_2$	10% Barden clay	--	>19 hrs.	--
1% $CuCl_2$	10% Celite	--	>22 hrs.	--
1% anh. $FeCl_3$	--	13-52 mins.	--	3 mins.
1% anh. $FeCl_3$	5% Hi-Sil	16-19 days	7-21 hrs.	4 mins.
1% anh. $FeCl_3$	10% Hi-Sil	>30 days	30-45 hrs.	100 mins.

Thermodynamic instability was more accurately and reproducibly evaluated by detection of an exotherm in a dual thermocouple test conducted as follows. A test mixture was prepared by intimately mixing the pesticide standard and the desired quantity of stabilizer. (The pesticide standard was thiodicarb containing sulfur as a synthesis impurity; no additional contaminants were added.) A thermocouple was placed into two grams of dried sample in a measuring vial. A second thermocouple was placed in the vial one inch above the surface of the mixture. The vial was then placed in a heating block and heated as quickly as possible to 160°C; the rate of heating was not important as long as it was reproducible and the mixture reached 160°C before the exotherm occurred for untreated pesticide. The time to exotherm for the mixture was compared to that for an untreated standard, i.e. one containing pesticide alone. Measurements for a single mixture of additive and pesticide were usually taken five to ten times to assure reproducibility. In all cases the pesticide was taken from the same batch to avoid differences in contamination levels that are often observed from one batch to the next. The time to exotherm was directly proportional to the thermal stability of the mixture.

As a group substantially non-alkaline inorganic compounds containing at least two oxygen atoms bound to a multivalent cationic atom are surprisingly effective at retarding or inhibiting the occurrence of the exotherm in sulfur-linked carbamate pesticides such as thiodicarb. Included in this group are the phosphorous acids; alkali metal

monobasic phosphates, metaphosphates, sulfites or bisulfites; alkali metal or alkaline earth aluminosilicates (zeolites or molecular sieves); alkali metal bicarbonates; and silicon dioxide in the form of silicas and silicates. The compounds that are especially effective at retarding the exotherm are sodium or potassium monobasic phosphate, sulfite or bisulfite; hexametaphosphate; and phosphoric acid. Mixtures of these compounds are also effective. The abilities of several of the preferred stabilizers to retard the exotherm in thiodicarb as measured in the dual thermcouple test described above are apparent from the results shown in Table III. These results indicate that potassium monobasic phosphate is an especially preferred stabilizer for thiodicarb.

TABLE III

TIME TO EXOTHERM FOR STABILIZED THIODICARB

Additive	Time to Exotherm (minutes)
--	54 (standard)
4% molecular sieves 4A	91
1% Na_2SO_3	75
5% Na_2SO_3	117
5% $NaHSO_3$	94
0.5% KH_2PO_4	>300
3% Na_2HPO_4	58

The decomposition of thiodicarb and the increasing concentration of methomyl have been monitored at 100°C in the presence of sodium monobasic phosphate (Table IV). Samples of

thiodicarb untreated and treated with varying amounts of sodium monobasic phosphate were maintained at 100°C for several days. They were periodically analyzed by standard HPLC methods for thiodicarb and methomyl. As thiodicarb concentration decreased, methomyl concentration increased. However, the results indicated that as the decomposition process continued, other products formed as well; the sum of the weight percentages of methomyl and thiodicarb became progressively smaller as decomposition proceeded. Increasing amounts of the monobasic phosphate appear to stabilize the thiodicarb as the decomposition reaction proceeds over several days; decomposition products, especially methomyl, accelerate the process. These results also support the hypothesis that bis alkylthio-alkylamino-N-alkyl carbamates undergo an autocatalytic decomposition process involving a number of sulfide species, also catalyze the process.

Stabilization of sulfur-linked bis alkylthio-alkylamino-N-alkyl carbamates may be achieved by incorporating the stabilizers of this invention in amounts ranging from 0.01 to 95 percent by weight of total mixture. Although the concentration of a particular inorganic stabilizer must be evaluated empirically, as a general rule preferred concentrations range from about 0.01 to about 10% by weight in solid formulations and from 0.0001% to about 6% by weight in liquid formulations. When the stabilizer is one of the above mentioned phosphate compounds, stabilization will be observed with as little as 0.01 to 2% by weight. Sulfite stabilizers are effective in the range of 0.1 to 5% by weight.

TABLE IV

THIODICARB DECOMPOSITION AND METHOMYL FORMATION IN THE PRESENCE OF NaH_2PO_4 at 100°C

Stabilizer		Day 0	1	2	3	4
--	Thiodicarb %	93.1	44.1	28	-	-
	Methomyl %	0.3	12.3	12.1	-	-
0.25% NaH_2PO_4	Thiodicarb %	93.1	82.0	78.8	54.5	-
	Methomyl %	0.3	2.5	5.7	12.2	-
0.5% NaH_2PO_4	Thiodicarb %	93.1	81.7	77.6	55.7	56.0
	Methomyl %	0.3	3.6	8.3	8.2	12.9
1% NaH_2PO_4	Thiodicarb %	93.1	81.6	85.9	84.8	63.9
	Methomyl	0.3	2.2	3.9	4.3	8.5

D. Formulations

The compositions of this invention may be applied as solids or as liquid dispersions or solutions to both field and turf to control pests. Application is by methods readily known to those skilled in the art. Effective amounts range from about 0.05 to about 20 lbs. per acre of active pesticide.

Formulations useful in the practice of this invention are solids, as wettable powders or dispersible granulars, and liquids, as solutions or dispersions. The preferred wettable powders and dispersible granular formulations comprise: (a) from about 1% to about 98% by weight of a bis alkylthio-alkylamino-N-alkyl carbamate pesticide; (b) from about 0.01% to about 10% by weight of a substantially non-alkaline inorganic compound containing at least two oxygen atoms bound to a multivalent cationic atom; (c) from about 0.01% to about 20% by weight of wetting agent; and (d) from about 1% to about 12% by weight dispersant.

Preferred liquid formulations comprise: (a) from about 0.01% to about 75% by weight of a bis alkylthio-alkylamino-N-alkyl carbamate pesticide; (b) from about 0.0001% to about 6% by weight of a substantially non-alkaline inorganic compound containing at least two oxygen atoms bound to a multivalent cationic atom; (c) from about 0.01% to about 20% by weight wetting agent; (d) from 0% to about 10% by weight dispersant; and (e) from about 5% to about 80% by weight inert liquid carrier. Suitable carriers include water, unsubstituted

aliphatic and aromatic hydrocarbons or analogues containing, for example, alkyl, halo or hydroxy substituents, fatty acids, and oils, such as linseed and cottonseed oil, derived from natural extracts.

Of the pesticides useful in this invention, the preferred compound is thiodicarb. The preferred oxygen-containing inorganic compounds are phosphoric acid and sodium or potassium monobasic phosphate, metaphosphate, sulfite or bisulfite.

Many wetting agents, anionic, cationic or nonionic, are available for these formulations. Illustrative wetting agents are alkali metal salts of fatty alkyl or alkenyl sulfates or sulfonates containing eight to twenty carbon atoms; alkali metal salts of alkylbenzyl or alkylnaphthyl sulfonates wherein the alkyl chain contains eight to twelve carbon atoms; ethoxylated alkylphenols wherein the alkyl groups contain eight to twelve carbon atoms; dialkylesters of sodium sulfonsuccinic acids wherein the dialkyl groups contain five to ten carbon atoms; or polyalkylene oxide modified dimethypolysiloxane in which the alkylene groups are ethylene or propylene or a mixture of both. Other suitable wetting agents may also be used.

Dispersants are materials which interact with solid ingredients in the formulations and the liquid medium that is used to suspend those solids for purposes of application. They must be soluble in that liquid phase and they usually behave as a binder for the solid powder or granular. Representative dispersants useful in the practice of

this invention include starches, alkali metal or alkaline earth salts of lignin sulfonates; and condensates of alkali metal alkylnaphthalene sulfonates and organic compounds containing one to three carbon atoms and at least one oxygen atom, such as the condensate of formaldehyde and sodium naphthalene sulfonic acid.

An additional component particularly useful in the formulations of this invention is an antifoaming agent. It prevents or reduces foam during the preparation of the powder or granulars and during dispersion and application of the composition. It also stabilizes the resulting dispersion and permits more rapid redispersion if coagulation of solids occurs in a dispersion. An especially useful antifoamer is a dialkylpolysiloxane. Particularly effective are dimethylpolysiloxanes formulated as emulsions or pastes. Such additives do not act as stabilizers for the pesticides.

Pesticidal formulations containing multiple pesticides are popular for the obvious reason of convenience--only one application is necessary to deposit all of the actives. While many multiple formulations are easily prepared simply by mixing all of the active ingredients, the formulations of this invention may require the presence of a compatability agent that prevents flocculation in the final solution or dispersion that is applied to the target plants. The presence of an additional, chemically unrelated pesticide such as parathion may destabilize a dispersion prepared for spray

application. The preferred compatability agents for these compositions are condensates of alkylene oxide and hydrophobic bases made by condensing an alkylene oxide with an alkylene glycol wherein all aklyl substituents contain from two to four carbon atoms. A particularly effective agent is a paste condensate of ethylene oxide with hydrophobic bases formed by condensing propylene oxide with propylene glycol.

A number of other well known ingredients can be incorporated into the wettable powders and dispersible granulars of this invention as the need arises, provided, of course, that they do not affect the ability of the inorganic compound to stabilize the pesticide or the stability and dispersibility or wettability of the powder or granular. These additives might include buffers, carriers or diluents, dyes, fragrances, humectants, thickeners, biocides and anti-evaporative agents.

The solid compositions of this invention can be prepared by various methods well known in the art, such as pan granulation, fluidized bed mixing and drying, spray drying, intensive mixing agglomeration, extrusion, compaction or pelletizing. For pan granulation and fluidized bed processes, a mixture of dry ingredients is prepared and transferred into the mixing/drying chamber that contains water and any liquid ingredients; the slurry is thoroughly mixed and then dried. Particles are then ground to a desired size. If a spray drying process is used, grinding of the mixture of dry ingredients or of the slurry is preferred.

The various processes yield solids containing a spectrum of particle sizes and moisture contents. A useful product is one which meets the particle size requirements for a particular application, which contains less than 5% by weight water, and preferably less than 2%, and which disperses well in water or oil. For granular compositions good dispersibility is obtained with particles retained on a U.S. Screen No. 100 (149 microns), and optimum particle stability is obtained with less than 2% moisture. Any particles that are too small, too large or too wet can be returned to the manufacturing or drying apparatus and recyled.

Preparation of the liquid compositions of this invention may be accomplished by methods known in the art. Useful dispersion formulations will not separate into liquid and solid phases during extended storage at ambient temperatures. To enhance stability the size of dispersed particles may be reduced by techniques, such as air and wet milling, known in the art.

The following examples are offered to illustrate useful formulations of this invention and to demonstrate the effects of various stabilizers.

EXAMPLE 1

To demonstrate the effect of a phosphate stabilizer in a dispersible granular, the following two formulations were prepared (by mixing ingredients in an aqueous slurry and spray drying to less than 2% water) and their thermal stability compared; (all values are percent by weight of the dry ingredients.

Formulation A (no thermal stabilizer)	Formulation B (thermal stabilizer)	Ingredient
87.4%	86.8%	thiodicarb
8.6	8.6	dispersant (sodium salt of sulfonated naphthylene formaldehyde condensate)
1.3	1.3	dispersant (starch)
2.5	2.5	wetting agent (sodium salt of sulfonated lauryl acid)
0.2	0.2	buffer (citric acid)
--	0.5	thermal stabilizer (NaH_2PO_4)
--	0.2	antifoamer (dimethyl-polysiloxane emulsion)
Time to Exotherm		
46 mins.	>120 mins.	

It is clear that as little as 0.5% NaH_2PO_4 greatly enhances the thermal stability of this formulation. Formulation B can be stored for much longer times at elevated temperatures (approximately 45-55°C) than Formulation A, and Formulation B is much less likely to decompose during drying than is Formulation A.

EXAMPLE 2

A dispersible granular stabilized with silica was prepared by mixing 86.5% by weight thiodicarb containing approximately 3% silica and 3% sulfur; dispersants (1.5% by weight starch, 6.8% by weight sodium salt of sulfonated naththalene

formaldehyde condensate, and 3.0% by weight polyalkylene glycol ether); wetting agent (1.0% by weight dioctyl ester of sodium sulfosuccinic acid); antifoamer (1.0% by weight magnesium stearate); and buffer (0.2% by weight citric acid). In this formulation stabilizer (i.e., silica) content was approximately 2.6% by weight. The mixture was ground to a powder of average particle size less than 10 microns and then transferred to a fluidized bed chamber for mixing with water and subsequent drying.

After screening the product to a range of -12 to +40 mesh (U.S. Sieve size), it had the following characteristics:

CIPAC suspendibility	76%
Time to exotherm	104 minutes

EXAMPLE 3

A very stable sample containing two stabilizers was prepared by slurrying, in water, the following ingredients (all weight percents are based on added weights of the ingredients except water): 86.1% thiodicarb containing 5% sulfur and 1.0% silica; 10.1% dispersant (sodium salt of sulfonated naphthalene formaldehyde condensate); 2.5% wetting agent (sodium salt of a sulfonated lauryl acid); 0.6% antifoaming emulsifier (dimethylpolysiloxane emulsion); and 0.7% thermal stabilizer (KH_2PO_4). The slurry is wet ground to pass through a No. 325 screen (U.S. Sieve size) and spray dried to a moisture content of less than 2%. Approximately 95% of the resulting granular has a

particle size distribution spanning the narrow range of -14 to +100 mesh (U.S. Sieve size).

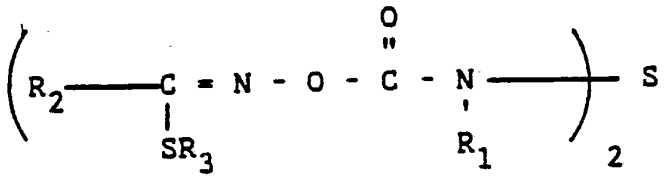
The granular within this particle size range exhibits the following characteristics:

CIPAC suspendibility 90%

Time to exotherm >120 minutes

What Is Claimed Is:

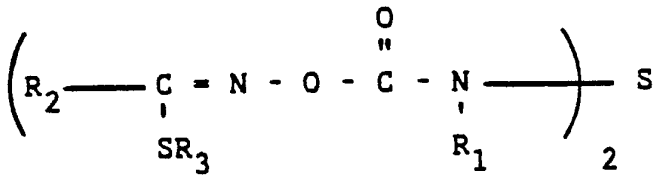
1. A method of retarding or inhibiting thermal decomposition of pesticides of the formula



wherein R_1 is alkyl containing from one to five carbon atoms; R_2 is alkyl, alkylthio, alkoxy, alkanoyl or alkoxycarbonyl, all of which may contain from one to five carbon atoms and which may be unsubstituted or aliphatically substituted in any combination with one or more cyano, nitro, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy or R_4R_5-NCO- groups; or R_2 is phenyl, R_4R_5-NCO- or $R_6CON(R_4)$, wherein R_4 and R_5 are individually hydrogen or alkyl, R_6 is hydrogen, alkyl or alkoxy; and R_3 is hydrogen, cyano, alkyl or alkylthio containing from one to five carbon atoms; provided that the total number of carbon atoms in R_2 and R_3 may not exceed eight and provided further that when R_2 is alkyl substituted with alkylthio, R_3 is alkyl, which comprises intimately mixing said pesticide with from about 0.01% to about 95% by weight of substantially non-alkaline inorganic compound containing at least two oxygen atoms bound to a multivalent cationic atom.

2. A pesticidal composition which comprises:

a. a pesticidally effective amount of an organic compound of the formula



wherein:

R_1 is alkyl containing from one to five carbon atoms;

R_2 is alkyl, alkylthio, alkoxy, alkanoyl or alkoxycarbonyl, all of which may contain from one to five carbon atoms and which may be unsubstituted or aliphatically substituted in any combination with one or more cyano, nitro, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy or R_4R_5-NCO- groups; or R_2 is phenyl, R_4R_5NCO- or $R_6CON(R_4)$; wherein:

R_4 and R_5 are individually hydrogen or alkyl;

R_6 is hydrogen, alkyl or alkoxy; and

R_3 is hydrogen, cyano, or alkyl or alkylthio containing from one to five carbon atoms;

provided that the total number of carbon atoms in R_2 and R_3 may not exceed eight and provided further that when R_2 is alkyl substituted with alkylthio, R_3 is alkyl; and

b. a substantially non-alkaline inorganic compound, containing at least two oxygen atoms bound to a multivalent cationic atom, in an amount effective to retard or inhibit thermal decomposition of said compound.

3. A pesticidal composition according to claim 2 wherein, in said organic compound, R_1 and R_3 are alkyl and R_2 is alkyl or alkylthio.

4. A pesticidal composition according to claim 3 wherein R_1, R_2 and R_3 are methyl.

5. A pesticidal composition according to claim 2 wherein said inorganic compound contains the phosphate, bicarbonate, silicate or sulfite anion.

6. A pesticidal composition according to claim 5 wherein said inorganic compound is a phosphorous acid; an alkali metal monobasic phosphate, metaphosphate, sulfite or bisulfite; an alkali metal or alkaline earth aluminum silicate; an alkali metal bicarbonate; silicon dioxide; or a mixture thereof.

7. A pesticidal composition according to claim 6 wherein said inorganic compound is sodium or potassium monobasic phosphate, sulfite or bisulfite; hexametaphosphate; phosphoric acid; or a mixture thereof.

8. A pesticidal composition according to claim 2 wherein said effective amount is from 0.01 to about 10% by weight.

9. A wettable powder or dispersible granular pesticidal composition according to claim 2 which comprises:

a. from about 2% to about 98% by weight of the organic compound of claim 2;
b. from about 0.01% to about 10% by weight of the inorganic compound of claim 2;
c. from about 0.01% to about 20% by weight wetting agent; and
d. from about 1% to about 12% by weight dispersant.

10. A pesticidal composition according to claim 9 wherein said organic compound is thiodicarb.

11. A pesticidal composition according to claim 9 wherein said inorganic compound is sodium or potassium monobasic phosphate, metaphosphate, sulfite or bisulfite; alkali metal bicarbonate; phosphoric acid; silicon dioxide; or a mixture thereof.

12. A pesticidal composition according to claim 9 wherein said wetting agent is an alkali metal salt of a fatty alkyl or alkenyl sulfate or sulfonate containing eight to twenty carbon atoms; an alkali metal salt of an alkylbenzyl or alkylnaphthyl sulfonate wherein the alkyl chain contains eight to twelve carbon atoms; an

ethoxylated alkylphenol wherein the alkyl group contains eight to twelve carbon atoms; a dialkylester of sodium sulfosuccinic acid wherein the dialkyl contains five to ten carbon atoms; or a polyalkylene oxide modified dimethylpolysiloxane in which the alkylene groups are ethylene or propylene or a mixture of both.

13. A pesticidal composition according to claim 9 wherein said dispersant is a starch, an alkali metal or alkaline earth salt of a lignin sulfonate, or a condensate of an alkali metal alkylnaphthalene sulfonate and an organic compound containing one to three carbon atoms and at least one oxygen atom.

14. A pesticidal composition according to claim 9 which also includes an antifoaming emulsifier.

15. A pesticidal composition according to claim 14 wherein said antifoaming emulsifier is a polymerized dimethylsiloxane or a mixture of an alkaline earth stearate with a polyalkylene glycol ether or with a sugar-free sodium sulfonate of Kraft lignin.

16. A pesticidal composition according to claim 9 which also includes a compatability agent.

17. A pesticidal composition according to claim 16 wherein said compatability agent is a condensate of alkylene oxide and hydrophobic base made by condensing an alkylene oxide with an

alkylene glycol wherein all alkyl substituents contain from two to four carbon atoms.

18. A pesticidal composition according to claim 17 wherein said condensate comprises ethylene oxide and a hydrophobic base made by condensing propylene oxide with propylene glycol.

19. A pesticidal composition which comprises from about 70% to about 95% by weight thiodicarb; from about 2% to about 3% by weight of sodium salt of sulfonated lauryl acid; from about 8% to about 15% by weight of a sulfonated naphthalene formaldehyde condensate; from about 1% to about 3% by weight of a dimethylpolysiloxane; and from about 0.5% to about 1.5% by weight sodium or potassium monobasic phosphate or phosphoric acid.

20. A pesticidal composition according to claim 19 which also includes a nonionic condensate of ethylene oxide and hydrophobic bases made by condensing propylene oxide with propylene glycol.

21. A liquid pesticidal composition according to claim 2 which comprises:

(a) from about 0.01% to about 75% by weight of bis alkylthio-alkylamino-N-alkyl carbamate pesticide;

(b) from about 0.0001% to about 6% by weight of a substantially non-alkaline inorganic compound containing at least two oxygen atoms bound to a multivalent cationic atom;

(c) from about 0.01% to about 20% by weight wetting agent;

(d) from 0% to about 10% by weight dispersant; and

(e) from about 5% to about 80% by weight inert liquid carrier.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 86/00776

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: A 01 N 47/24; A 01 N 25/22

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	A 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	GB, A, 2005140 (DU PONT) 19 April 1979 see examples 4,6-8 --	1-21
X	GB, A, 2079154 (DU PONT) 20 January 1982 see examples 3-4 --	1-21
X	US, A, 4297370 (E.J. JOBOCZENSKI) 27 October 1981 see example 3 --	1-21
X	EP, A, 0056739 (UNION CARBIDE) 28 July 1982 see page 6, lines 19-20; page 8, example 1 --	1-21
X	Journal of Agricultural and Food Chemistry vol. 27, no. 5, September/October 1979, American Chemical Society, (Washington D.C., US) M. Chiba: "Use of Ammonium or Potassium dihydrogen Phosphate to Protect Pesticides in Spray Mixtures Prepared with Alkaline Waters", pages 1023-1026	1-21

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
28th July 1986	09 SEP 1986
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	L. ROSSI

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 86/00776 (SA 12982)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/08/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A- 2005140	19/04/79	BE-A-	870790	27/03/79
		NL-A-	7809781	30/03/79
		FR-A,B	2404398	27/04/79
		DE-A-	2842281	05/04/79
		LU-A-	80289	29/10/79
		JP-A-	54059324	12/05/79
		AU-A-	4021878	03/04/80
		AU-B-	524402	16/09/82
GB-A- 2079154	20/01/82	FR-A-	2485882	08/01/82
		AU-A-	7238781	07/01/82
		DE-A-	3126369	22/07/82
US-A- 4297370	27/10/81	None		
EP-A- 0056739	28/07/82	AU-A-	7966082	26/08/82