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ΚΥΠΡΙΑΚΟ ΓΡΑΦΕΙΟ ΔΙΠΛΩΜΑΤΩΝ ΕΥΡΕΣΙΤΕΧΝΙΑΣ

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(54) **Encapsulated pesticidal composition**

(57) A method of encapsulating a pesticide for the purpose of reducing the phytotoxicity to plants while essentially maintaining pesticidal activity. The product is produced by drying a mixture of pesticide on a particulate carrier suspended in a polymer latex.

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SPECIFICATION

A pesticidal composition and a method for its preparation

This invention relates to a method of encapsulating a pesticide for the purpose of reducing the phytotoxicity to plants while essentially maintaining pesticidal activity. The invention also relates to an encapsulated pesticidal composition useful in such method, produced by drying a mixture of pesticide on a particulate carrier suspended in a polymer latex.

Various methods for encapsulating are known. The following references disclose conventional methods:

U.S.P. 2,800,457, Green et al., July 23, 1957, teaches a method of making oil-containing capsules by emulsifying oil in an aqueous sol using two hydrophilic colloidal materials having opposite electric charges, cooling the mixture and recovering the gelled product.

U.S.P. 2,800,458, Green, July 23, 1967, discloses a salt-coacervation method for encapsulating oil using gellable hydrophilic colloidal material.

U.S.P. 3,015,128, Somerville, January 2, 1962, deals with a centrifugal encapsulating apparatus for covering filler material such as kerosene with a medium such as a mixture of polyvinyl alcohol and sodium alginate in a water/glycerol solvent.

U.S.P. 3,016,308, Macaulay, January 9, 1962, teaches rupturable capsules containing a liquid using either a non-ionizable water-soluble or an hydrophobic water-insoluble film former.

U.S.P. 3,423,489, Arens et al., January 21, 1969, deals with an encapsulating process for liquid materials using two separate streams, one for the encapsulating material and the other for the liquid filler.

U.S.P. 3,429,827, Ruus, February 25, 1969, discloses a process for encapsulating substances such as liquids or dispersions in a shell based on condensation polymers using two separate polymer reactants, such polymer being formed at the interface of the substance within the reaction medium.

Many chemicals useful for the control of pests such as insects, acarids, fungi, etc. may cause phytotoxicity to the leaves of plants or trees sensitive to such chemicals when applied at pesticidally effective concentrations. The results are loss of green leaf surface or partial defoliation of the plant as well as reduction of yield and possible loss of plants. It is important to maintain pesticidal activity of such chemicals while reducing the phytotoxicity of the active material to the plants.

It has been found that the phytotoxic effects of such chemicals can be greatly reduced or completely eliminated when the pesticide is applied to a particulate carrier material and the resulting carrier-pesticide combination is subsequently encapsulated with a polymer material. Concentrations of pesticide on carrier materials may typically be from 5 to 80 percent, preferably 20 to 65 percent by weight, largely depending on the ability of the carrier to absorb the chemical. Typical carrier material is a finely divided powder such as diatomaceous earth, in which category is included equivalent materials derived from diatomaceous earth, having a small particle size (e.g. surface area of 5 to 200 m^2/g, preferably 10 to 95 m^2/g). The pesticide may be a liquid or solid but is preferably liquid. The pesticide may be an acaricide (e.g., a sulfite acaricide), insecticide, fungicide, etc.

The pesticide-on-carrier particles are ordinarily dispersed in water using a mixture of dispersing and wetting agents such as sodium lignosulfonate and non-ionic surfactants for producing an aqueous dispersion of pesticide on the carrier. Other surfactants which can be used are polymerized salts of alkyl naphthalene sulfonic acid and the sodium sulfosuccinates. Latex is then added to the water-surfactant (pesticide-carrier) slurry with agitation sufficient to disperse the carrier and pesticide particles throughout the latex. If necessary, such latexes may be further stabilized by the addition of suitable stabilizers such s polyvinyl alcohol or hydroxyethyl cellulose. The latex particle size may typically vary from 0.1 to 25 microns, preferably 0.5 to 8 microns, in diameter.

Some thickening of the surry occurs when the latex is combined with the pesticide-on-carrier water slurry. Usually, water is added to the slurry reducing the final solids to about 30%, which results in a slurry viscosity of from 25 to 250 centipoise.

A dry powdery product is obtained by drying the latex-carrier pesticide suspension, typically by passing the suspension through a spray dryer, for example at a temperature of from 120 to 220°C. The choice of spray drying equipment is not critical athough spray dryers where the suspension is introduced from the top into the hot air stream are frequently more desirable.

When a mixture of relatively large and small particle size latexes is used, a more uniform polymer coating of the carrier/pesticide may be achieved.

Additional surfactants may be added to the particles for better wetting and dispersion when the product is used in a spray solution to be applied to a crop.

A typical process for making the product may be summarized as follows:

1. Mix carrier and liquid or solid pesticide at about room temperature to 100°C maximum.

2. Add carrier/pesticide particles to water containing dispersing and/or wetting agents while agitating.

3. Add latex [containing polyvinyl acetate polymer or other suitable polymer] to suspension achieved by step (2) with agitation.

4. Pass product of step (3) through spray dryer.

Optionally, a portion of the dispersing/wetting agents may be added to the product achieved by step (1). Additional surfactant can be mixed with the product of step (4) to assure good dispersion of the product when used in a spray application.

Example 1

Preparation of Encapsulated Acaricide.

(A) 2-[4-(1,1-dimethylethyl)phenoxy]cyclohexyl 2-propynyl sulfite (a liquid, also known as propargite) at about 50°C is sprayed onto diatomaceous earth (surface area 95 m^2/g) in a ribbon blender. Surfactants indicated in the recipe below are then added while agitating and the mixture is hammer milled. Eight separate preparations are prepared and combined. The following recipe (wherein parts are expressed by weight) is used:

Propargite, 84.6% active	286 parts
Diatomaceous earth	240 parts
Highly purified sodium lignosulfonate	2 parts
Octylphenoxy polyethoxy-ethanol absorbed on magnesium carbonate	2 parts
Polymerized sodium salts of alkyl naphthalene sulfonic acid	2 parts

The product (A) contains 46.7% of active acaricide.

(B). The above mixture is further modified using the recipes below (wherein amounts are expressed in grams):

Sample Number:	*1*	*2*	*3*	*4*
Acaricide on diatomaceous earth (A)	404.9	404.9	404.9	
Highly purified sodium lignosulfonate	9.0	3.5	4.5	
Octyl phenoxy polyethoxyethanol absorbed magnesium carbonate	3.0	1.2	1.5	
Polymerized sodium salts of alkyl naphthalene sulfonic acid	3.0	1.2	1.5	
Dioctyl ester of sodium sulfosuccinic acid	–	1.2	–	
Polyvinyl acetate latex (PVAC) 55% solids	131.0	175.0	87.0	
Water	1100.0	1100.0	1100.0	
PVAC, weight percent	14.9	19.2	10.4	
Acaricide				36.7
Sodium N-methyl-N-palmitoyl taurate				1.5
Propylene glycol				2.0
Sodium alkyl naphthalenesulfonate				1.0
Salts of lignosulfonic acid				4.0
Diatomaceous earth (surface area 95 m^2/g)				7.1
Diatomaceous earth (surface area 10–20 m^2/g)				13.0
Attapulgus clay				34.7

Under agitation, the surfactants are added to the water until dissolved. The acaricide on diatomaceous earth is then added as rapidly as the slurry permits. The polymer latex is added with stirring. The slurry is spray-dried at 110 ml per minute at an input temperature of 120°C. After drying, sample 1 contains 37.7% active ingredient, sample 2 contains 35.0%, while sample 3 contains 39.3% acaricide. Sample 4, which is a control sample that is outside the invention, included for purposes of comparison only, is prepared by spraying the acaricide into a mixture of the fillers and then adding surfactants. Hammer milling is used to make the product uniform. The resulting product contains 31% active acaricide.

Acaricidal Test

(C) The ability of these formulations to kill two-spotted spider mites is determined using the following procedure: Cowpea (Vigna sinensis Germaine's Blackeye #5) are planted, 3 seeds per pot. When grown to first trifoliate stage, each pot is thinned to the best two plants. These are sprayed with a JGA 502 DeVilbiss (trademark) spray gun for 20 seconds each pot. Spray solutions are made using addition of water to bring solutions to concentration indicated in Table I. 1, 8, 14 and 28 days after spraying, two-spotted spider mites are applied to each leaf inside a "Tanglefoot" (trademark) circle on the top of each leaf. The number of live mites remaining seven days after application is counted. The percent control is calculated using the following equation:

$$\% \text{ control} = 100 \times \frac{\left[\text{number of live mites in untreated check} - \text{number of live mites/sample}\right]}{\text{number of live mites in untreated check}}$$

The results are summarized in Table I.

Table I

Composition	Rate ppm	% Control 1 day	8 day	14 day	28 day
1	500	–	96	87	86
	100	81	47	71	43
	20	18	40	26	20
	5	0	–	–	–
2	500	–	100	96	80
	100	83	77	59	50
	20	19	69	40	29
	5	0	–	–	–
3	500	–	100	100	100
	100	85	85	75	67
	20	60	70	56	49
	5	7	–	–	–
4	500	–	100	100	100
	100	100	89	98	56
	20	86	50	37	33
	5	60	–	–	–

The results in Table I show that samples 1, 2 and 3 are as effective in controlling two-spotted spider mites as the untreated control 4 over a 28 day period.

Herbicidal Test

(D) The effect of these treatments on the phytotoxicity of acaricide to cowpeas is tested as in (C) except mites are not applied. Higher concentrations of acaricide are used to exaggerate possible phytotoxic effects. The samples are rated 7 days after spraying. The degree of damage produced is determined, and the results shown in Table II are obtained.

Table II

	% Damage Primary Leaves			Damage Trifoliate Leaves		
Sample No.	ppm: 8000	2000	500	8000	2000	500
1	15	5	1	Mod.	Trace	Slight
2	15	2	0	Mod.	Slight	Trace
3	10	3	0	Mod.	Slight	Trace
4 (Control)	95	20	0	Sev.	Mod/Sev.	Slight

The results in Table II show that the encapsulating material substantially reduces phytotoxic damage to leaves by the acaricide. 95% damages means essentially all of the green leaf surface has been destroyed.

(E) Potted Tioga strawberries are sprayed with a spray containing one pound active propargite per acre in 32 gallons of water. One half pint of adjuvant surfactant per 100 gallons of water is included in each treatment. Ten replicate pots are used for each treatment. Five days after treatment the plants are rated for phytotoxicity. On a 1 to 10 scale (1 = least damage), the results whown in Table III are obtained:

Table III

Sample No.	Mean phytotoxicity damage
1	5.0
2	5.5
3	6.0
4 (Control)	9.0

The data in Table III shown considerable improvement in damage reduction to strawberries when the encapsulated samples 1, 2 and 3 are used compared with the non-encapsulated control 4.

Example 2

Preparation of Encapsulated Acaricide

Production scale equipment is used for sample preparation applying various amounts of encapsulating polymer. The acaricide-on-carrier is prepared by spraying hot (about 50°C) acaricide into diatomaceous earth in a Littleford-Lodigé (trademark) mixer. The following recipe is used:

(A)

Propargite, 86.5%	18.5 pounds
Diatomaceous earth	16.0 ,,
Highly purified sodium lignosulfonate	0.2 ,,
Dioctyl ester of sodium sulfosuccinic acid	0.2 ,,

After all of the propargite has been sprayed into the diatomaceous earth, the surfactants are added. An assay of 47 percent of acaricide is determined.

(B) In the same manner as in Example 1(B), a slurry is prepared containing the pesticide-on-carrier mixture. Encapsulation is carried out using polyvinyl acetate latex (55% solids) and sufficient water to provide the specified percentage of active acaricide, according to the following recipes:

Sample	5	6	7	8	9
Propargite on DE (See A), pounds	22.5	21.25	20.0	17.5	13.75
Polyvinyl acetate-dry, pounds	2.5	3.75	5.0	7.5	11.75
Highly purified sodium lignosulfonate, grams	35.0	95.0	78.0	125.0	104.00
Dioctyl ester of sodium sulfosuccinic acid, grams	9.0	–	–	–	–
Octyl phenoxy polyethoxy ethanol absorbed on magnesium carbonate, grams	–	32.0	23.0	40.0	34.0
Polymerized sodium salts of alkyl naphthalene sulfonic acid, grams	–	32.0	23.0	40.0	34.0
Polymer wt.-%	10.0	15.0	20.0	30.0	45.0
Active acaricide wt.-%	44.3	42.5	40.0	33.6	27.5

Acaricial Test

(C) Acaricidal tests are conducted using the procedure outlined in Example 1 (C) except for the one-day test. The control of the spider mites is calculated as before. Tests results are shown in Tale IV.

Table IV

	% Control					
	8 day			28 day		
Sample No.	500 ppm	100 ppm	20 ppm	500 ppm	100 ppm	20 ppm
5	100	100	72	100	87	45
6	100	100	81	100	80	25
7	100	100	91	93	58	7
8	100	98	86	95	70	18
9	100	100	79	100	27	5
4 (Control)	100	98	77	100	55	45

The results in Table IV clearly indicate that the encapsulated products are essentially as effective in killing spider mites as the untreated control material (Sample 4).

Herbicidal Test

(D) The phytotoxic effects of these preparations to cowpeas is shown in Table V. The acaricide is applied as in Example 1 (D). The amount of damage by the acaricide is rated 7 days after application.

Table V

	Primary Leaves			Trifoliates		
	% Damage			Damage		
Sample	8000 ppm	2000 ppm	500 ppm	8000 ppm	2000 ppm	500 ppm
5	60	15	3	Sev	Slight	Trace
6	15	3	1	Mod. Sev.	Slight	0
7	0	1	0	Mod.	Trace	0
8	5	0	0	Mod. Sl.	Trace	0
9	0	0	0	Trace	0	0
4 (Control)	95	45	15	Sev.	Sev. Mod.	Slight

Considerable phytotoxicity to primary leaves (i.e. bronzing and almost complete destruction of the green leaf surface) is evident at 500 ppm to 8000 ppm of the untreated control 4. Damage to the trifoliates (which are just emerging when the sprays as applied) represent curling, twisting and stunting of the leaf growth. These results show that as the polymer weight percent is increased the phytotoxic effect of the pesticide is considerabl reduced.

Example 3

The samples prepared in Example 2 are evaluated on 3-year old Bartlett pear trees. The entire leaf surface is treated, and each solution is applied to runoff at the two applications rates used. Phytotoxicity readings are taken 14 days after spraying, with the results shown in Table VI.

Table VI

	Phytotoxicity	
	Application rate-ppm	
Sample No.	300	600
5	Trace-Sl.	Trace-Sl.
6	Trace	Trace
7	0	Trace
8	0	0
9	0	Trace
4 (Control)	Moderate- Slight defoliation	Moderate-Severe Moderate Defoliation

Bartlett pears are very sensitive to this acaricide. Defoliation may occur even at a low rate normally used to control spider mites. Reduction in phytotoxicity is found even at the lowest polymer weight percentage. Samples 7, 8 and 9 having higher polymer weight percentage exhibit essentially no damage, whereas non-treated controls 4 cause moderate to severe damage.

Example 4

This example demonstrates the effects of using a blend of large and small particle size polyvinyl acetate latexes.

(A) Preparation of Encapsulated Acaricide

The acaricide on diatomaceous earth (DE) used in Example 2(A) is used. The slurry preparation technique is the same as in 2 (B). The following preparations are made:

Sample	10	11	12	13	14	15
Propargite on DE, lbs.	21.25	19.0	22.5	12.7	17.5	25.2
Polyvinyl acetate Latex A, lbs.	3.75	1.705	2.5	1.3	7.5	9.8
Polyvinyl acetate Latex B, lbs.	–	1.705	–	1.3	–	9.8
Highly purified sodium lignosulfonate, g	23.0	150.0	35.0	65.0	125.0	160.0
Octyl phenoxy polyethoxy ethanol absorbed on mg carbonate, g	–	50.0	–	23.00	40.0	53.0
Polymerized sodium salts of alkyl naphthalene sulfonic acids, g	–	50.0	–	23.0	40.0	53.0
Dioctyl ester of sodium sulfosuccinic acid, g	6.0	–	9.0	–	–	–
Acaricide, % weight	41.6	38.5	44.3	33.5	41.6	34.3

Polyvinyl acetate latex A (55% solids) has a particle sizle of 2.8 microns and latex B (55% solids) has a particle size of 0.5–1.5 microns.

(B) Phytotoxicity to catelopes is demonstrated using the method of Example 1 (D). The results obtained at a rate of 1 pound of active acaricide per acre are shown in Table VII.

Table VII

	Phytotoxicity to Cantelopes
Sample Latex	Mean Damage
10 A	4.13
11 A & B	3.93
12 A	5.20
13 A & B	5.00
14 A	2.73
15 A & B	1.47
4 (Control)	8.60

The results in Table VII show reduced phytotoxicity resulting when a mixture of large and small particle size latexes are used rather than a single particle size latex.

CLAIMS

1. A method for encapsulating a pesticide comprising the steps of:
(a) absorbing said pesticide on a solid particulate carrier;
(b) dispersing the product of step (a) in water;
(c) adding a latex to the dispersion of step (b); and
(d) drying the suspension obtained from step (c).

2. A method according to claim 1 wherein the said pesticide is a liquid pesticide, and the said drying is spray drying.

3. A method according to claim 1 or claim 2 wherein said carrier is diatomaceous earth and said latex is polyvinyl acetate latex.

4. A method according to any of the preceding claims wherein the dispersion obtained by step (b) contains dispersing and/or wetting agent.

5. A method according to any of the preceding claims wherein step (c) is carried out while agitating the dispersion

6. A method according to any of the preceding claims wherein said pesticide is an acaricide.

7. A method according to claim 6 wherein said acaricide is a sulfite acaracide.

8. A method according to Claim 7 wherein said sulfite is 2-[4-(1,1-dimethylethyl)phenoxy]cyclohexyl 2-propynyl sulfite.

9. An encapsulated pesticidal composition comprising a solid carrier having absorbed thereon a liquid pesticide, the pesticide-on-carrier material being covered by a solid polymer.

10. A composition according to claim 9 wherein said polymer is polyvinyl acetate.

11. A composition according to claim 9 or claim 10 wherein said carrier is diatomaceous earth.

12. A method according to claim 1 and substantially as described herein.

13. A method for encapsulating a pesticide substantially as described in any of the Examples.

14. An encapsulated pesticidal composition according to claim 9 and substantially as described herein.

15. An encapsulated pesticidal composition substantially as described in any of the Examples.

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